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LEOPOLD GMELIN

VOL. XVI

ORGANIC CHEMISTRY.

VOL. X.

ORGANIC COMPOUNDS CONTAINING FROM 24 TO 34 ATOMS OF CARBON

TRANSLATED BY

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(VOL. X OF ORGANIC CHEMISTRY.)

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Oxynitroazo-nucleus $C^{26}N^2XH^9O^2$.

Oxybromonitroazo-nucleus $C^{26}N^2XBrH^8O^2$.

Oxychloronitroazo-nucleus $C^{26}N^2XClH^8O^2$.

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ADDENDA.

ERRATA.

		Line.				
15	....	15 from bottom, *for*	Phloretin	*read*	Phlorizin.	
129	....	20 from top,	,,	H^{25}	,,	H^{15}.
130	....	12 from top,	,,	H^{11}	,,	H^{13}.
135	....	11 from top,	,,	O^4	,,	O^8.
182	....	7 from top,	,,	C^{26}	,,	C^{28}.
183	....	12 from top	,,	C^{26}	,,	C^{28}.
244	...	9 from top,	,,	H^{34}	,,	H^{14}.
269	....	8 from top,	,,	H^{20}	,,	H^{24}.
271	....	2 from top,	,,	H^{36}	,,	H^{26}.
377	.	2 from top,	,,	$C^{76}H^{10}O^{12}$	,,	$C^{70}H^{70}O^{12}$.

GLUCOSIDES (*continued*).

Glucosides with 16 at. Carbon in the Copula.

Indican.

$$C^{52}NH^{31}O^{34}.$$

E. Schunck. *Phil. Mag.* [4] 10, 73; abstr. *J. pr. Chem.* 66, 321;
Chem. Centr. 1856, 50; *Lieb. Kopp's Jahresb.* 1855, 659. — *Phil. Mag.*
[4] 14, 288; *Chem. Centr.* 1857, 957; *Kopp's Jahresb.* 1857, 564.
— *Phil. Mag.* [4] 15, 29, 117, and 283; abstr. *J. pr. Chem.* 73, 268;
74, 99 and 174; *Chem. Centr.* 1858, 225; *Kopp's Jahresb.* 1858, 465.
— *Manchester Soc. Mem.* 14, 239; abstr. *J. pr. Chem.* 75, 376.

The constituent of woad which forms indigo-blue (xiii, 35), occurs
in human urine both healthy and diseased, and, when present in
considerable quantity, causes the urine, after spontaneous fermentation,
or on addition of acids, to deposit sometimes indigo-blue (xiii, 35;
Handbuch, Zoochem. vii, ?), sometimes indirubin [the latter perhaps identical
with Heller's *Urrhodin* (*Handbuch, Zoochem* 312 and 389), and Golding Bird's
Purpurin (*ibid* 389)]. It may be detected by precipitating the urine
with basic acetate of lead, collecting the precipitate which forms in the
filtrate on addition of ammonia, and decomposing it with cold dilute
acids, the filtrate then depositing, first, indigo-blue, then indirubin,
and afterwards other products of the decomposition of indican.
(Schunck, *Manchester Soc. Mem.* 14, 239; abstr. *J. pr. Chem.* 75, 376.)
All human urine contains indican, which is likewise found in the blood
of man, and in the blood and urine of the ox. When a few cubic
centimetres of urine are poured upon ¼ the volume of oil of vitriol
and then agitated, a colour varying from lilac to dark indigo-blue
is produced, arising from the decomposition of indican. When serum
of blood separated from the clot is precipitated with neutral acetate of
lead, the filtrate boiled, filtered again and mixed with ammonia, the
scanty precipitate, if treated while yet moist with excess of sul-
phuric acid, exhibits a red colour, due to the presence of indican.
Ether removes the colour after supersaturation with ammonia. (Carter,
Edinb. Medic. J. Aug., 1859. *Rép. Chim. pure,* 2, 239.)

Preparation. From woad-leaves, carefully dried and pulverised while warm. 1. The leaves are exhausted with cold alcohol in a displacement apparatus; the green tincture is precipitated with alcoholic sugar-of-lead and a little ammonia-water, and the pale green precipitate after washing with cold alcohol is decomposed under water by a stream of carbonic acid; it then loses its colour, and yields a yellow solution, which, when freed from dissolved lead by sulphuretted hydrogen and evaporated over oil of vitriol, yields indican. — 2. The tincture prepared with cold alcohol is concentrated, after addition of a little water, by passing a stream of air over it at the common temperature; the fat which separates is removed by filtration; the filtrate shaken up with recently precipitated cupric hydrate; the liquid again filtered; the filtrate freed from dissolved copper by hydrosulphuric acid; and the liquid separated from the sulphide of copper is evaporated at the temperature of the air. From the residual brown syrup, cold alcohol dissolves out the indican, leaving undissolved a brown viscid mass which contains oxindicanin. By mixing the alcoholic solution with 2 vol. ether, further products of decomposition are precipitated, whilst the indican is obtained by evaporating the filtrate. When thus prepared it still retains a little fat.

Properties. Yellow or yellow-brown syrup, which cannot be dried without decomposing. It has a slightly bitter and repulsive taste, and an acid reaction. According to the analysis of the lead-salt, its formula is $C^{52}NH^{31}O^{34}$ or $C^{52}NH^{33}O^{36}$. (Schunck.)

The following are the products formed during the evaporation of an aqueous solution of indican :—

a. *Oxindicanin.* — The mass which separates by spontaneous evaporation as described at page 2, is purified by repeated solution in water and precipitation with alcohol; it contains 8 at. oxygen more than indicanin (p. 5). Brown viscid gum having a nauseous taste. Combustible. — By boiling with dilute sulphuric acid, it is resolved into indifuscin and indiglucin.

$$C^{40}NH^{23}O^{32} = C^{24}NH^{10}O^9 + C^{12}H^{10}O^{12} + 4CO^2 + 3HO.$$
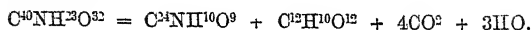
From its aqueous solutions, neutral acetate of lead throws down a dirty yellow precipitate, and the filtrate yields with ammonia a second light yellow precipitate, containing, on the average, 23·02 p. c. C., 2·2 H., 1·2 N., 49·54 PbO. and 24·04 O., and answering, after deduction of the lead-oxide, to the formula $C^{40}NH^{23}O^{32}$.

b. *Oxindicasin.* — Produced when an aqueous solution of indican is evaporated by heat, the indican, according to Schunck, being first converted, with separation of indiglucin, into indicanin, the latter, with absorption of oxygen, into oxindicanin, and this last, being resolved, with assumption of water, into oxindicasin and indiglucin :

$$C^{40}NH^{23}O^{32} + 3HO = C^{28}NH^{16}O^{23} + C^{12}H^{10}O^{12}.$$
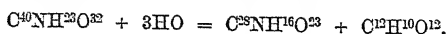
It is purified like oxindicanin, which it also resembles. The yellow lead-salt (precipitated with excess of acetate of lead ?) contains $C^{28}NH^{16}O^{23},4PbO$.

c. *Indicasin.* — The liquid filtered from the lead compound of

oxindicasin, which contains excess of lead-acetate, yields, when treated with a large quantity of alcohol, a pale yellow precipitate $= C^{28}NH^{20}O^{23}, 6PbO$. The organic substance in the precipitate appears to be a mixture of indicasin (which is related to oxindicasin in the same manner as indicanin to oxindicanin) and oxindicasin in equivalent proportions, united with 8 at. water. (Schunck.)

Decompositions. 1. Indican decomposes even when gently *warmed*, and at a stronger *heat* swells up and emits vapours which condense to an oil solidifying partially in the crystalline form. — 2. When heated in aqueous solution it is resolved into leucine, indicanin, and indiglucin. The products formed during the evaporation are described above. — 3. In contact with *soda-ley* or *baryta-water*, indican is resolved into indicanin and indiglucin :

$$C^{52}NH^{31}O^{34} + 2HO = C^{40}NH^{23}O^{24} + C^{12}H^{10}O^{12}.$$
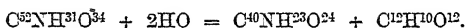
A solution of indican left for several days in contact with soda-ley, yields, with acids, indirubin, produced from the indicanin ; after longer standing, indiretin is likewise obtained, and in some cases the latter is the only product.

4 Indican is decomposed by dilute *acids* in the cold, and more quickly when heated. The decomposition is induced by tartaric and oxalic acids, as well as by mineral acids, less easily by acetic acid. Aqueous indican mixed with dilute sulphuric acid, becomes turbid on standing, and deposits blue flocks, the formation of which ceases after 24 hours. The filtrate, after standing for some time, and still more when heated, deposits a brown powder, while leucine and indiglucin remain in solution, together with certain volatile products, viz., carbonic, formic, acetic, and perhaps propionic acid, which escape when the liquid is heated.

The substance insoluble in water is a mixture of six different bodies. On exhausting it, first with cold, then with warm dilute soda-ley. *indihumin, indifuscin,* and *indiretin* are dissolved ; the residue yields to alcohol, α- or β-*indifulvin* and *indirubin,* together with residues of indifuscin, while *indigo-blue* (xiii, 35) remains in solution. Instead of indifuscin, *indifuscone* is sometimes obtained. Schunck gives the following formulæ :—

a. Formation of indigo-blue or its isomer, indirubin, and of indiglucin :

$$C^{52}NH^{31}O^{34} + 4HO = C^{16}NH^{5}O^{2} + 3C^{12}H^{10}O^{12}.$$
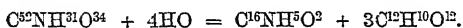
Part of the indigo-blue is said to split up into leucine, formic acid, and carbonic acid :
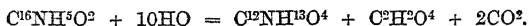
$$C^{16}NH^{5}O^{2} + 10HO = C^{12}NH^{13}O^{4} + C^{2}H^{2}O^{4} + 2CO^{2}.$$

b. Formation of α-indifulvin, indiglucin, and formic acid :

$$C^{52}NH^{31}O^{34} + 5HO = C^{28}NH^{10}O^{3} + 2C^{12}H^{10}O^{12} + 3C^{2}H^{2}O^{4}.$$

c. Formation of β-indifulvin, indiglucin, formic acid, and carbonic acid :

$$2C^{52}NH^{31}O^{34} + 7HO = C^{44}N^{2}H^{19}O^{3} + 4C^{12}H^{10}O^{12} + 5C^{2}H^{2}O^{4} + 2CO^{2}.$$
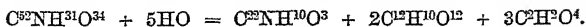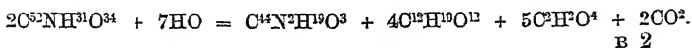
d. Formation of indihumin, indiglucin, propionic acid, and carbonic acid :

$$C^{52}NH^{31}O^{34} + 4HO = C^{20}NH^9O^6 + 2C^{12}H^{10}O^{12} + C^6H^6O^4 + 2CO^2.$$
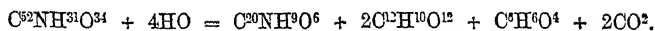
e. Formation of indifuscone, indiglucin, acetic acid, and carbonic acid :

$$C^{52}NH^{31}O^{34} + 3HO = C^{22}NH^{10}O^5 + 2C^{12}H^{10}O^{12} + C^4H^4O^4 + 2CO^2.$$
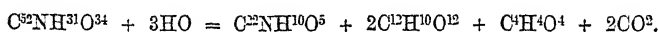
f. Formation of indiretin, indiglucin, carbonic acid, and water :

$$C^{52}NH^{31}O^{34} = C^{36}NH^{17}O^{10} + C^{12}H^{10}O^{12} + 4CO^2 + 4HO.$$
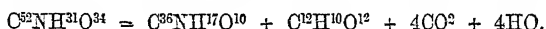
Combinations. Indican dissolves in *water* with yellow colour.

With Lead-oxide. — Neutral acetate of lead forms with alcoholic solution of indican, a sulphur-yellow precipitate which increases on addition of ammonia. Aqueous indican is precipitated only by an ammoniacal solution of the neutral acetate of lead. When alcoholic indican is mixed with a small quantity of alcoholic neutral acetate of lead, the dirty yellow precipitate removed, and excess of lead-acetate added to the filtrate, a light yellow precipitate is formed, which, after washing with alcohol, drying in vacuo, and afterwards on the water-bath, constitutes the lead-salts 1 and 2. The liquid filtered therefrom deposits, on addition of a little ammonia, another precipitate, which after similar treatment constitutes the salts 3 and 4. (Schunck.)

	1.	2.	3.	4.
C	20·45	15·54	19·21	18·17
N	0·79	0 71	0 82	0·72
H	3·06		2·11	2·00
O	16·47		17 58	17·12
PbO	59·23	68·73	60·28	61·99
	100·00		100·00	100·00

After deduction of the Lead-oxide.

a.

52 C		49 60
N		2·22
31 H		4·92
34 O		43·26

$$C^{52}NH^{31}O^{34} \dots\dots\dots 100·00$$

b.	1.	2.	3.	4.
52 C	48·22	50·15	49·69	48·36	47·80
N	2·16	1·93	2·27	2·06	1·89
33 H	5·10	5·05		5·31	5·26
36 O	44·52	42·87		44·27	45·05
$C^{52}NH^{31}O^{34},2HO$	100·00	100·00		100·00	100·00

Indican is soluble in *alcohol* and in *ether.*

Indicanin.

$$C^{40}NH^{23}O^{24} = C^{16}NH^5O^2, 2C^{12}H^9O^{11}.$$
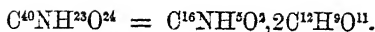
Schunck. *Phil. Mag.* [4] 15, 183; abstr. *J. pr. Chem.* 74, 99.

Produced, together with indiglucin, by the reaction of aqueous alkalies or baryta-water on indican (see page 3):

$$C^{52}NH^{31}O^{34} + 2HO = C^{40}NH^{23}O^{24} + C^{12}H^{10}O^{12}.$$
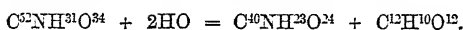
Indican is left in contact with baryta-water; the liquid is precipitated with dilute sulphuric acid; and the filtrate is freed from excess of sulphuric acid by carbonate of lead, from lead by sulphuretted hydrogen, and evaporated in a stream of air at mean temperature. The residue is dissolved in alcohol; the solution is mixed with twice its volume of ether, which precipitates indiglucin; and the filtrate is left to evaporate. The residue frequently contains also products of decomposition. (p. 3) Yellow or brown bitter syrup.

Heated on platinum-foil, it swells up strongly and leaves charcoal. — By *dry distillation* it yields a brown oil in which white needles form. — When boiled with *acids*, it yields indiglucin and indirubin, and if impure, likewise indiretin and indifuscin. Formation of indirubin:—

$$C^{40}NH^{23}O^{24} + 2HO = C^{16}NH^5O^2 + 2C^{12}H^{10}O^{12}.$$
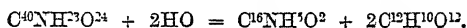
Gives off ammonia when boiled with *soda-ley*.

Lead-compound. — Aqueous indicanin forms a slight precipitate with neutral acetate of lead; from alcoholic indicanin, an alcoholic solution of neutral acetate of lead throws down a copious sulphur-yellow precipitate, soluble in excess of the lead-acetate and precipitable by ammonia.

		at 100°.				Schunck.
40	C	240	....	21·06	....	21·27
	N	14	....	1·22	....	1·35
23	H	23	....	2 01	....	2 09
24	O	192	....	16 88	....	16·78
6	PbO	672	....	58·83	....	58·51

$C^{40}NH^{23}O^{24}, 6PbO$ .... 1141 .... 100·00 .... 100·00

Indicanin dissolves in *alcohol* and in *ether*.

Appendix to Indican and Indicanin.

1. *Indihumin* $C^{20}NH^9O^6$. Perhaps identical with indigo-brown xiii, 48). — *Formation and Preparation of Indihumin and the following products.* —Indican is heated with dilute sulphuric acid; the flocks which separate are collected (the solution which runs off being preserved for the preparation of indiglucin, as described at page 302, vol. xv), washed with cold water, and treated first with cold, then with warm dilute soda-ley, which dissolves one portion, and leaves another containing α- and β-indifulvin, indirubin, and indigo-blue. The alkaline

solution is precipitated with hydrochloric acid, the precipitate collected and washed, and treated with boiling ammonia, which dissolves indifuscin and indiretin, and leaves *indihumin*. The ammoniacal solution neutralised with acetic acid, yields a precipitate of *indifuscin*, and an additional quantity of this product is precipitated from the filtrate by alcoholic sugar-of-lead. The *indiretin* which still remains in solution is separated by ammonia in combination with lead-oxide, and contaminated with indifuscin; it is separated from the lead-oxide by treating the precipitate with acetic and then with hot hydrochloric acid, and purified by repeated solution in alcohol, which leaves the indifuscin undissolved.

The mixture of α- and β-indifulvin, indirubin, and indigo-blue, insoluble in dilute soda-ley, gives up to boiling alcohol everything excepting the indigo-blue. The purple-brown alcoholic solution mixed with ammonia and alcoholic sugar-of-lead, deposits residues of substances soluble in soda-ley; and on separating these, then adding excess of acetic acid, distilling off the alcohol, and diluting largely with water, purple-brown flocks are obtained, from which, when purified with dilute soda-ley, a small quantity of cold alcohol extracts *indifulvin*. On boiling the residue with an alkaline solution of protochloride of tin, filtering hot, and exposing the filtrate to the air, a purple-red deposit is formed, consisting of *indirubin*. This is washed with water and dissolved in alcohol. The portion insoluble in the alkaline solution is a mixture of indirubin and indifulvin.

Indihumin is obtained but sparingly, and not on all occasions. It is a brown powder, containing 62·86 p. c. C., 7·19 N., 4·71 H., and 25·24 O, answering to the formula $C^{20}NH^9O^6$ (calc. 62·82 C., 7·33 N, 4·71 H., 25·14 O.)—Burns without melting when *heated*.—Dissolves in boiling *nitric acid*, forming a yellow solution, which, when evaporated, leaves an orange-yellow residue. — Insoluble in *water* and in *alcohol*, but dissolves in aqueous *alkalis*, forming a brown liquid, from which it is precipitated by acids.

2. *Indifuscin* and *Indifuscone*, $C^{24}NH^{10}O^9$ and $C^{22}NH^{10}O^{52}$? Produced most abundantly when the indican has been previously in contact with oxygen (see *Oxindicanin* p. 2). — Brown powder resembling indihumin; contains 59·4 to 67·5 p. c. C., 5·78 to 7·12 N., and 29·12 to 20·23 O., so that it appears to agree, sometimes with one, sometimes with the other of the formulæ just given. — When *heated*, it emits vapours, with an odour of burning turf, and yields an oily distillate. *Burns* without fusion. — Colours *chromic acid* green; with boiling *nitric acid*, it yields oxalic and picric acids. Dissolves in *oil of vitriol* with brown colour, giving off sulphurous acid when heated. — Insoluble in boiling water; dissolves easily in alcoholic *ammonia*, whence it is precipitated in brown flocks by acids; also in aqueous *alkalis* and *alkaline carbonates*, and is precipitated therefrom by *metallic* salts. Sparingly soluble in boiling *alcohol*.

3. *Indifulvin*. Obtained of various composition as α-indifulvin ($C^{22}NH^{16}O^3$) and β-indifulvin ($C^{44}N^2H^{19}O^3$). Brittle, friable, reddish-yellow resin, which was once obtained as α-indifulvin containing 73·40 C., 8·12 N., 5·39 H., and 13·09 O (calc. 73·33 C., 7·77 N., 5·55 H., and 13·35 O.), and another time as β-indifulvin, containing 78·32 p. c. C., 8·56 N., 5·81 H., and 7·31 O. (calc. 78·80 C., 8·35 N., 5·67 H, and 7·18 O.)

— Melts when heated, *burns* with flame and leaves charcoal. *Heated* in a glass tube, it gives off a strong-smelling vapour, condensing to a brown oil, which solidifies in the crystalline form. Dissolves in *oil of vitriol* with green-brown colour, and chars when heated. By ordinary *nitric acid*, it is scarcely attacked, even at the boiling heat; but it dissolves in fuming nitric acid, and is precipitated by water in orange-yellow flocks. By heating and evaporating the liquid, a yellow resin is obtained, together with crystals soluble in water, and different from oxalic acid. — Slowly decomposed by *chromic acid*. — Does not dissolve in aqueous *alkalis*, even at the boiling heat, or on addition of grape-sugar, or protochloride of tin.

4. *Indiretin.* $C^{36}NH^{17}O^{10}$. Dark-brown shining resin, which at $100°$—$190°$, contains, on the average 66·04 p. c. C., 3·83 N., 5·57 H., and 24·56 O. (calc. 66 05 C., 4 28 N., 5·19 H., and 24 48 O.) — When *heated* on platinum foil, it melts, burns with a yellow, smoky flame, and leaves charcoal. By *dry distillation* it gives off strong-smelling vapours, and yields an oily distillate. Dissolves in *oil of vitriol* with brown colour, and chars when heated. With boiling *nitric acid*, it forms resin and picric acid. — Dissolves easily in aqueous *alkalis*, and with brown colour in *ammonia*, being precipitated therefrom by *baryta-, lime-,* and *silver-salts.* Precipitated from the alcoholic solution by *neutral acetate of lead*, and partially by *cupric acetate.*

5. *Indirubin.* $C^{16}NH^{5}O^{2}$. Isomeric with indigo-blue (xiii, 35), and, perhaps, identical with indigo-red (xiii, 45). Obtained in small quantity by decomposition of indican, more abundantly from Indian woad-leaves, by immersing them in a boiling alkaline solution of protochloride of tin, the liquid then depositing indirubin on exposure to the air. The product thus ʻobtained is purified by dissolving it in alkaline protochloride of tin, and treating it, after reprecipitation, with caustic soda, acids, and water, and then recrystallised from alcohol. — Long, purple, metallic-shining needles, which appear red by transmitted light, and when heated volatilize in red vapours and sublime. In the impure state, it is a brown-red amorphous powder. Contains 72·78 p. c. C., 10·50 N., 4·16 H., and 12·56 O., agreeing with the formula $C^{16}NH^{5}O^{2}$. — It dissolves with purple colour in *oil of vitriol*, and is partially precipitated therefrom by water. — Cold *nitric acid* dissolves it with purple colour, but on applying heat, decomposition takes place, attended with formation of resin and picric acid. — It is but slightly altered by a mixture of *chromate of potash* and dilute *sulphuric acid*, even at the boiling heat. — With *chlorine* under water, it forms a blue amorphous resin soluble in alcohol. Heated with *soda-lime*, it gives off an odour of benzoin, together with alkaline vapours, which partly condense to needles. — Insoluble in aqueous alkalis, but dissolves easily on addition of *protochloride of tin* or *grape-sugar*. — From the yellow-solution, acids throw down dirty yellow flocks, which acquire a purple colour on exposure to the air, and impart a fast purple dye to cotton-wool immersed in the liquid and afterwards exposed to the air. It is not precipitated from the alcoholic solution by ammoniacal *sugar of lead*. Its sulphuric acid solution imparts a fine colour to wool, cotton and silk.

Glucosides with 18 at. Carbon in the Copula.

Phloretin.

$$C^{30}H^{14}O^{10} = C^{18}H^{8}O^{4}, C^{12}H^{6}O^{6}.$$
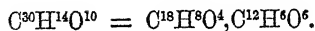
STAS.   *Ann. Chim. Phys.* 69, 367 ; *Ann. Pharm.* 30, 200.
G. ROSER.   *Ann. Pharm.* 84, 178 ; *Pharm. Centr.* 1850, 778 ; *Compt. Chim.* 1850, 306.
H. HLASIWETZ.   *Wien. Akad. Ber.* 17, 382 ; *J. pr. Chem.* 67, 105 ; *Ann. Pharm.* 96, 118.

Formation.   XV, 347.

Preparation.   When phlorizin is dissolved in dilute sulphuric (hydrochloric, oxalic, or other) acid, and the solution is heated for some time to 90°, phloretin is deposited as a crystalline powder. It is purified by washing and recrystallisation (Stas). The complete decomposition of phlorizin requires many days' digestion in the water-bath.

Properties.   White crystalline laminæ having a sweet taste. Does not give off any water at 160°, melts at 180°, and decomposes at a higher temperature (Stas).

				Stas.		Roser. mean.
30 C	180	....	65·69	....	64·73	.... 65·19
14 H	14	......	5·11	....	5·33	..... 5·26
10 O	80	.. ...	29·20	.....	29 94	.. ... 29·55
$C^{30}H^{14}O^{10}$	274	....	100 00	.. ...	100·00	.... 100·00

So, according to Strecker (*Ann. Pharm.* 71, 184). Stas gave the formula $C^{24}H^{11}O^{8}$; Marchand $C^{52}H^{26}O^{17}$; Liebig $C^{30}H^{15}O^{10}$. Strecker's calculation was founded on the experiments of Roser (p. 14).

Decompositions.   1. When pulverised phloretin is treated with *bromine* under ether, a mixture of ter- and quadri-brominated phloretin is produced, which by renewed treatment with bromine, is wholly converted into quadribromo-phloretin (Schmidt & Hesse, *Ann. Pharm.* 119, 103).
Bromine heated in excess with phloretin decomposes it, forming a kneadable mass, partly soluble in boiling water. The aqueous solution deposits on cooling : *a.* White interlaced needles, which melt between 97° and 104°, solidify in the crystalline form on cooling, give off 2·8 p. c. water at 90°, and then contain 31·1 p. c. carbon and 2·3 hydrogen ;—*b.* Pale reddish needles with 9·5 p. c. water, after removal of which at 95° they contain 24·4 p. c. carbon, and 1·7 hydrogen ; both dissolve in ammonia-water with brown colour, changing to purple, and finally again to brown on exposure to the air. When the crystals *a* and *b* are again treated with bromine-water, and the mixture is heated to expel excess of bromine, a solid mass is obtained on cooling, containing 21·1 p. c. carbon, and 1·2 hydrogen. Hence, Schmidt & Hesse regard *a*, *b*, and the mass obtained from them, as a mixture of mono- and ter-bromophloroglucin (XV, 68). (Schmidt & Hesse, *Ann. Pharm.* 119, 103.)

By chlorate of potash and hydrochloric acid, phloretin is converted into a yellow resin, soluble in alcohol, the reaction not being attended with formation of chloranil (xi, 196). (Hofmann. *Ann. Pharm.* 52, 65.)

2. *Chromic acid* converts phloretin into formic and carbonic acids (Stas). — 3. Cold dilute *nitric acid* dissolves phloretin, and decomposes it after prolonged action. Strong nitric acid decomposes it immediately, with evolution of carbonic acid and nitric oxide, and formation of oxalic acid and a dark brown substance. The latter dissolved in aqueous alkali, after washing with water, and precipitated by an acid, constitutes Stas's phloretic acid (different from the phloretic acid of Hlasiwetz, xiii, 308), a flea-brown, velvety, uncrystallisable powder, containing, on the average 54·6 p. c. C., 3·76 H., 5·8 N., and 35·84 O. This phloretic acid decomposes at 150° with evolution of nitric oxide; is converted by strong nitric acid into oxalic acid and a trace of bitter substance; dissolves in oil of vitriol with blood-red colour; also in alkalis; is insoluble in water, and in dilute acids; but soluble in alcohol and wood-spirit. (Stas.) Mulder (*J. pr. Chem.* 32, 330) regards this body as aprocrenic acid containing ammonia; Stas gave the formula $C^{24}NH^{10}O^{12}$; Liebig $C^{30}NH^{12}O^{15}$ or $C^{24}NH^{9}O^{12}$; Weltzien (*Org. Verb.* Braunschw. 1860, p. 492) regards it as nitrophloretin $C^{30}XH^{14}O^{10}$.—4. By boiling and evaporation with strong *potash-ley*, phloretin is resolved into phloretic acid (xiii, 308) and phloroglucin (xv, 65). (Hlasiwetz.) — 5. Phloretin is not decomposed by potassio-cupric tartrate (Roser).

Combinations. Phloretin is almost insoluble in cold, very sparingly soluble in boiling *water*. It dissolves without decomposition in concentrated *acids* (Stas).

It absorbs *ammonia gas*, becoming hot, melting, and taking up 13·5 to 14·18 p. c. of its weight of ammonia (3 at. = 15·33 p. c. NH³), without elimination of water. After saturation, the compound solidifies in the amorphous state. — The solution formed by pouring concentrated aqueous ammonia on phloretin, deposits, after a few seconds, small yellow shining grains, which give off ammonia when exposed to the air, or when their aqueous solution is heated, and precipitate metallic salts (Stas).

Phloretin dissolves in aqueous *alkalis* without alteration, if not exposed to the air. In contact with the air, oxygen is absorbed and an orange-coloured body is formed, perhaps the same as that yielded by solutions of phlorizin in contact with the air. The solutions have a sweet taste (Stas).

Lead-compound. — Phloretin does not give off water when heated with oxide of lead. — The compound is prepared by precipitating excess of phloretin-ammonia with basic acetate of lead, and drying the precipitate at 140° in a current of air (Stas).

30	C	182		22·89		20·08
14	H	14		1·76		1·69
10	O	80		10·06		9·93
5	PbO	519		65·29		68·30
	$C^{30}H^{14}O^{10},5PbO$	795		100·00		100·00

Silver-compound. — Nitrate of silver throws down from aqueous phloretin-ammonia a precipitate which, after washing and drying in the dark, contains 26·6 p. c. silver-oxide, and 73·4 p. c. phloretin, but is easily decomposible. (Stas.)

Phloretin dissolves in all proportions in hot cencentrated *acetic acid*, and separates in shining crystalline grains on cooling. — It dissolves easily in *alcohol* and *wood-spirit*, is nearly insoluble in cold, and sparingly soluble in boiling *ether*. (Stas.)

Alpha-phloretin.

$$C^{66}H^{32}O^{28} = C^{18}H^8O^4,4C^{12}H^6O^6.$$
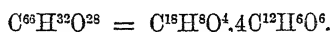
HLASIWETZ.   *Ann. Pharm.* 119, 199.

Not named by Hlasiwetz. — Belongs to Berthelot's quadrisaccharides (xv, 318).

A mixture of phloretic acid (xiii. 308) and dry phloroglucin (xv. 65) heated to 150° in an air-bath, melts together, and gives up water.   If kept for six hours between 160° and 180°, it deposits a granular mass, and ultimately becomes quite solid.   The brown mass, when boiled with water, dissolves slowly, and the solution, even before it is quite cold, deposits crystalline scales, which may be purified by washing with warm water, and recrystallisation from boiling water, with help of animal charcoal.

Nearly colourless microscopic laminæ, having a rough taste, with sweetish after-taste.   Neutral.   Unalterable at 150°.   Colours aqueous *sesquichloride of iron* violet.

							Hlasiwetz.
66	C	396	......	60·73		......	60 06
32	H	32	......	4·91		......	4·99
28	O	224	......	34 36		......	34 95
$C^{66}H^{32}O^{28}$		652	......	100·00		......	100·00

Quadribromophloretin.

$$C^{30}Br^4H^{10}O^{10} = C^{18}BrH^7O^4,C^{12}Br^3H^3O^6?$$
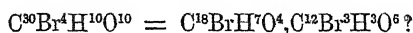
O. SCHMIDT & HESSE.   *Ann. Pharm.* 119, 103.

Formation and Preparation. 1. When finely pulverised phloretin is covered with ether, and bromine added to the mixture cooled from without, the bromine is absorbed, with evolution of heat, and a mixture of ter- and quadri-bromophloretin is formed, which, after removal of the ether and the resulting hydrobromic acid, may be completely converted into quadri-bromophloretin by renewed treatment with bromine at a gentle heat.   The product is boiled with water ; the residue is dissolved in boiling alcohol ; the solution precipitated with water ; and the pale yellow crystalline precipitate is purified by boiling with weak and recrystallisation from boiling alcohol. — 2. Phlorizin treated with bromine under ether likewise yields quadri-brimophloretin, a mixture of mono- and poly- bromophloro-glucin being formed at the same time.

Properties. Small, pale, yellow needles, which do not lose weight at 100°, are decolorised by animal charcoal, but soon turn yellow again.

		Crystals.				Schmidt & Hesse. mean.
30	C	180	....	30·51	....	30·35
4	Br	320	....	54·23	....	54·00
10	H	10	....	1·69	....	1·95
10	O	80	..	13·57	....	13·70
$C^{30}Br^4H^{10}O^{10}$		590	....	100·00	....	100·00

Melts between 205° and 210°, acquiring at the same time a dark red colour, and decomposing with effervescence. — It dissolves, with yellow colour, in aqueous *ammonia* and *soda*, the ammoniacal solution turning brown after a while. In boiling *lime-water* it turns violet, and forms an amorphous violet substance.

Insoluble in boiling *water*, sparingly soluble in boiling *alcohol*, easily in *ether*.

Phlorizin.

$$C^{42}H^{24}O^{20} = C^{12}H^{10}O^{10},C^{30}H^{14}O^{10}.$$
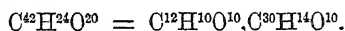
L. DE KONINCK. *Mémoire sur le phloridzin*, Louvain, 1836; abstr. *Ann. Pharm.* 15, 75, and 258; *J. pr. Chem.* 8, 88.

STAS. *Ann. Chim. Phys.* 69, 367; *Ann. Pharm.* 30, 192; *J. pr. Chem.* 17, 273.

MULDER. *J. pr. Chem.* 17, 299 and 304; 18, 256; 32, 330.

G. ROSER. *Ann. Pharm.* 74, 178; *Compt. chim.* 1850, 306; *Pharm. Centr.* 1850, 778.

Also *Phlorrhizin* and *Phloridzin*, from φλοιός bark and ῥίζα root. Discovered by De Koninck and Stas in 1835.

Sources. In the root-bark of the apple, pear, cherry, and plum tree, less abundantly in the bark of the stem and branches (De Koninck). In the bark of the bird-cherry tree (Boullier, *J. Chim. méd.* 17, 520). Also in the leaves of the apple tree (Diehl, *Jahrb. pr. Pharm.* 2, 140), but not in the bark of the almond, peach, apricot, or nut tree (De Koninck). In the root-bark of the red currant tree, Eng (*Pharm. Viertelj.* 3, 9) found a bitter extractive matter, which, according to Wittstein, appears to agree with phlorizin. Old apple trees, no longer capable of bearing fruit, likewise contain phlorizin ; but the root-bark of trees which have been dead for some time, contain but little of it, and that of partly decayed trees none at all (Diehl, *Jahrb. pr. Pharm.* 2, 143). The root-bark collected in January contains more than that which is collected in February or in the spring, when the sap appears to carry the phlorizin from the root into the leaves (Diehl, *Repert.* 66, 225). Little or no phlorizin is obtained from the dry root-bark (De Koninck).

Preparation. Most advantageously from the root-bark of the apple tree, which contains less colouring matter than that of other trees. 1. The fresh

bark (which turns red if left exposed to the air, and should therefore be immersed in water as soon as it is peeled off) is twice boiled with a quantity of water sufficient to cover it, the decoction then poured off and left to itself for 24 to 36 hours; it then deposits phlorizin in crystals. The mother-liquors yield an additional quantity, but impure. De Koninck boils for 4 or 5 hours, then a second time for 1 to 2 hours; according to Boullier (*J. Chim. méd.* 13, 184 and 366), half-an-hour's boiling is sufficient, longer boiling yielding a less pure product. — Phlorizin may be obtained from the leaves of the apple tree, after precipitating the decoction with alcohol, whereby gum and malate of lime are obtained. (Diehl.)

2. The fresh root-bark is covered with weak alcohol, and heated for 7 or 8 hours to 50° or 60°; the liquid then decanted, the residue twice treated with alcohol; the whole of the tinctures subjected to distillation, and the residue cooled; phlorizin then crystallises out. (De Koninck.)

Purification. By recrystallisation with help of animal charcoal. Or, according to Roser, the crude phlorizin is dissolved in hot water; the liquid boiled with a little gelatin, whereupon the foreign bodies settle down as a viscid brown mass, on the sides of the vessel; and the decanted liquid is mixed with a small quantity of alum and neutralised with chalk, which throws down the remaining impurities, together with the alumina. The filtrate then yields nearly colourless crystals, which may be completely purified by addition of a few drops of solution of basic acetate of lead, and recrystallised from water slightly acidulated with acetic acid. — Impure phlorizin is easily decolorised by chlorine. (Weigand, *Jahrb. pr. Pharm.* 1, 83.)

The fresh root-bark of the apple-tree treated by the first method yields 3 p. c., according to the second, 5 p. c. phlorizin (De Koninck). Diehl, by the first method, obtained from the root-bark of a very old tree, 1·4 p. c.; from the leaves of the apple tree, about $\frac{8}{10}$ p. c. phlorizin.

Properties. Crystallised phlorizin heated to 100° gives off water, and is converted into anhydrous phlorizin, which melts at 100° (De Koninck), at 106°, and completely at 109° (Stas) to a colourless liquid, which, when further heated to 130°, hardens again to a mass resembling gum-arabic. It melts again between 158° and 160°, but suffers no loss of weight even at 185° (Stas). Phlorizin melted at 106° and solidified at 130°, crystallises unaltered from solution in water; that which has been melted at 160°, still yields with acids and lead-oxide, the decomposition products of phlorizin, but it no longer dissolves readily in water, and separates from its solution without crystalline form. To obtain it crystallised again, the solutions must either be boiled or left to evaporate spontaneously. (Stas). Similar results were obtained by De Koninck. — Phlorizin, after dehydration, does not absorb water from moist air (De Koninck). Phlorizin tastes sweetish at first, then bitter, finally astringent (De Koninck); first pungently sweetish, then persistently, but not intensely bitter, and with scarcely perceptible astringency (Geiger); not at all astringent (Buchner). Tastes indistinctly bitter, then sweet (Stas). Inodorous, neutral. — Molecular rotatory power to the left: $[\alpha]r$ for crystallised

phlorizin = 39·98° (Bouchardat, *Compt. rend.* 18, 299). See also Wilhelmy, *Lieb. Kopp's Jahresb.* 1850, p. 176.

		Dried.		Petersen.		Erdmann.		Erdmann & Marchand.
42 C	....	252	.... 57·79	.... 56·15	....	56·90	....	56·31
24 H	....	24	.... 5·51	.... 5 81	....	5·89	....	5·61
20 O	....	160	.... 36·70	.... 38·04	....	37 21	....	38·08
$C^{42}H^{24}O^{20}$....		436	.... 100·00	.... 100·00	....	100 00	....	100·00

	Marchand.		Mulder.	Stas.
	earlier.	*later.*	*mean.*	*at* 100°—160°.
C	56·37	.... 56·89	.... 56 68	.... 57·47
H........	5·55	. ... 5·88	.... 5·74	.... 5·67
O	38·08	.... 37·23	.... 37·58	.... 36·86
	100·00	. .. . 100·00	.... 100·00	.... 100·00

Earlier formulæ: $C^9H^5O^4$ (Petersen, *Ann. Pharm.* 15, 178); $C^{18}H^9O^7$ (Erdmann, *J. pr. Chem.* 8, 100); $C^{28}H^{17}O^{14}$ (Erdmann & Marchand, *J. pr. Chem.* 15, 305); $C^{12}H^7O^6$ (Marchand, *J. pr. Chem.* 16, 357); $C^{21}H^{13}O^{10}$ (Mulder, *J. pr. Chem.* 17, 299; and Marchand, *J. pr. Chem.* 17, 308); C^3-$H^{18}O^{10}$ (Stas); $C^{42}H^{25}O^{20}$ (Liebig, *Ann. Pharm.* 30, 217; Berzelius, *Jahresb.* 19, 535; Roser). This last formula differs from that of Strecker (*Ann. Pharm.* 74, 181), now universally adopted, only by containing 1 at. hydrogen more.

Decompositions. 1. Phlorizin which has been melted at 160° begins to boil briskly at 200°, giving up water and being converted into a dark-red substance, and decomposes completely at about 350°. Crystallised phlorizin, thus treated, loses, on the whole, 15·3 p. c. water (Stas). (8 at = 15·25 p. c. HO). Phlorizin boils at 177°, decomposes at 197°, giving off at the same time, a small quantity of benzoic acid (? Gm.) pyroacetic spirit, carbonic acid, and a brown heavy oil (De Koninck).

The body produced with loss of 16·3 to 16·5 p.c. water, on heating (crystallised) phlorizin to 235°, is Mulder's *Rufin* or *Rutilin*, which, according to him, is allied to the product obtained by the action of oil of vitriol on phlorizin, and to the bodies formed under similar circumstances from salicin (xv, 434), and differs from these several bodies only by the amount of water which it contains. — When phlorizin is heated in the oil-bath to 190°, it begins to effervesce, from escape of aqueous vapour, and in half an hour the residue assumes the appearance of a resin having a fine red colour, Mulder's *rufin*, which is brittle, friable, soluble with deep orange colour in alcohol, but insoluble in ether. This resin is dissolved and decoloured by boiling water, the solution becoming milky as it cools. It is insoluble in hydrochloric acid, dissolves in warm nitric acid, with decomposition, and in oil of vitriol, with formation of Mulder's *rufisulphuric acid* (see below), which is decolorised by water, but forms with lime a red soluble salt = $C^{14}H^7O^5,CaO,2SO^3$. It dissolves with fine red colour in aqueous ammonia and potash, and is precipitated by dilute sulphuric acid. This rufin contains, according to Mulder, 61·18 p.c. C., and 5·25 H., corresponding to the formula $C^{14}H^7O^5$, and is formed as represented by the equation: $2C^{21}H^{13}O^{12}$ (Mulder's formula for crystallised phlorizin) = $3C^{14}H^7O^5$ + 9HO. The numbers calculated from Mulder's analyses (or in consequence of misprints?) are 59·59 and 60·45 C., 5·24 H.; the formula $C^{42}H^{20}O^{16}$ requires 63 p.c. C., and 5 H. (Kr.)

2. Anhydrous *sulphuric acid* colours phlorizin yellow, then brown, and chars it without giving off sulphurous acid (De Koninck). Oil of vitriol decomposes it, with carbonisation, and forms a red solution (De Koninck). Crystallised phlorizin, on which oil of vitriol is poured, turns yellow, and water then produces a white precipitate (Buchner); if the temperature rises to 30°, the mixture turns red, but is decolor-

ised by water. Phlorizin treated with oil of vitriol at 60° to 70°, no longer loses its red colour on addition of water, being converted into *Ruji-* or *Rutili-sulphuric acid* (Mulder).

If the red solution obtained by the action of oil of vitriol on phlorizin at 30° be diluted and neutralized with chalk, alcohol throws down from the red-brown filtrate a gelatinous precipitate of rufisulphate of lime, containing 29 01 p.c. C., 3·4 H., 30·41 SO³ and 14 52 CaO, and resembling the salt obtained in like manner from salicin. Mulder estimates the carbon higher, supposing that some of the carbonic acid remained with the lime, and gives the formula $2C^{14}H^7O^5.SO^3,2Aq + 3CaO.SO^3$. The same salt is obtained, according to Mulder, by the action of oil of vitriol on the rufin formed from phlorizin by heat.

Dilute sulphuric acid (also phosphoric, hydriodic, hydrochloric acids) dissolves phlorizin in the cold without alteration (De Koninck, Stas). Aqueous sulphuric acid of the strength of 1 per cent. does not alter the rotatory power of the solution in 48 hours (Bouchardat). The solution, heated to 80° or 90°, becomes turbid, and deposits crystalline phloretin (p. 8) while glucose remains in solution (Stas):

$$C^{42}H^{24}O^{20} + 2HO = C^{30}H^{14}O^{10} + C^{12}H^{12}O^{12} \text{ (Strecker)}.$$
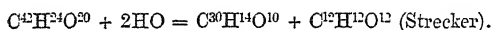
Respecting the sugar produced in this reaction, see xv, 317.

When 1 gr. dried phlorizin is heated over the water-bath with 20 grs. water and 50 drops of dilute sulphuric acid, the maximum quantity of sugar, amounting, on the average,[*] to 41·76 p. c., is formed in four days, 60·46 p. c. phloretin being separated at the same time (Roser) (calc. 41 28 p. c. $C^{12}H^{12}O^{12}$ and 62 84 phloretin).

3. Strong *nitric acid* acts immediately on phlorizin, evolving nitrous gas and carbonic acid, and producing oxalic acid, together with a dark-red substance, Stas's phloretic acid (p. 9), which remains undissolved. Strong nitric acid produces a black-brown resin, which dissolves with dark red colour when the liquid is heated, and disappears on further boiling, with decoloration and evolution of nitrous gas (Petersen). Dilute nitric acid dissolves phlorizin at first but without alteration, forming a pale yellow solution, which, if left overnight, deposits a yellowish precipitate. A mixture of aqueous phlorizin, with a small quantity of dilute sulphuric acid, slowly turns brown, and yields a dark brown jelly (De Koninck). According to Buchner (*Repert.* 66, 224), a solution of phlorizin in nitric acid deposits, on standing, slender, needle-shaped crystals, sparingly soluble in water and alcohol, and neutral after washing.

4. Strong *hydrochloric acid* converts phlorizin into a dirty red, amorphous substance without dissolving it (De Koninck).

5. When phlorizin is triturated with $\frac{1}{10}$ of its weight of *iodine*, a greyish violet mass is formed, from which water separates black flocks. (Vogel, *N. Br. Arch.* 16, 155). — When phlorizin is covered with ether and bromine is dropped into the liquid, as long as it is decolorised thereby, the phlorizin dissolves completely; and on evaporating the solution, boiling the residue with dilute sulphuric acid (to decompose phlorizin), and recrystallising, quadribromophloretin (p. 10) is obtained. (Schmidt & Hesse, *Ann. Pharm.* 119, 105). — *Chlorine*, bromine and iodine evolve heat from dry phlorizin, and convert it into a brown

viscid resin; aqueous chlorine added to aqueous phlorizin forms a yellow precipitate (De Koninck). — When phlorizin is treated with *chloride of lime*, carbonate of lime and resins are formed, but neither chloranil, nor a volatile oil, nor crystals (Stenhouse, *Ann. Pharm.* 55, 4). Aqueous chloride of lime colours aqueous phlorizin light yellow at first, brown after some days, without precipitation (De Koninck). With *chlorate of potash* and *hydrochloric acid*, phlorizin behaves like phloretin (Hofmann, p. 9). Phlorizin distilled with sulphuric acid and bichromate of potash, does not yield any oil analogous to salicylous acid (Mulder); but it yields formic acid (Strecker).

6. Phlorizin, saturated with *ammonia* and exposed to the air in the moist state, acquires successively an orange-red, purple-red, and dark blue colour, and is converted into phlorizem-ammonia (p. 16). By the continued action of the air, and especially of oxygen-gas, the blue compound is destroyed, and converted into a brown-red bitter substance, sparingly soluble in water (Stas). On evaporating the brown-red solution, redissolving, and precipitating with neutral acetate of lead, the nearly colourless filtrate exhibits the reactions of sugar, and leaves, after removal of the lead-oxide, a hygroscopic insipid mass, which burns with the odour of sugar (Illasiwetz, *Ann. Pharm.* 119, 211). — 7. Boiling *potash-ley* of 45° B., forms with phlorizin a black acid, acting, in fact, like an acid, and producing glucose, and then further decomposing this substance. — This solution of phlorizin in dilute aqueous alkalis rapidly absorbs oxygen from the air; changes from yellow to red-brown; loses its original alkaline reaction, and is found to contain carbonic acid, acetic acid, and a red-brown colouring matter (Stas). — 8. On distilling phlorizin with *lime*, the same products are obtained as in the dry distillation of phlorizin *per se*, but neither benzoic nor carbonic acid (De Koninck). — 9. Phlorizin does not reduce *potassio-cupric tartrate* (Roser). Mixed with cupric sulphate and potash-ley, it forms a green precipitate, which is coloured blue by excess of potash without dissolving, and when heated turns green, and finally brown (Lassaigne, *J. Chim. méd.* 18. 417).

10. No sugar is formed by *emulsin*. (Rochleder, *Wien. Akad. Ber.* 24, 32).

Combinations. — *With Water.* *Hydrated Phloretin.* White silky needles often united in radiate groups; by slow crystallisation from dilute solutions it is obtained in large flattened needles having a pearly lustre (De Koninck, Stas). Sp. gr. 1·4298 at 19° (De Koninck). Gives off water of crystallisation at 100°, more quickly at 110°, 7 p. c. (De Koninck); 6·82 (Erdmann and Marchand); 7·7 (Marchand); 7·89 (Mulder); 7·8 p. c. (Stas). 4 at. = 7·63 p. c. HO.

	Crystallised.		Mulder. mean.		Marchand.		Stas. mean.		Roser.
42 C	252	53·39	52·53		52·75		53·24		53·95
28 H	28	5·93	6·08		6·32		6·12		6·17
24 O	192	40·68	41·39		40·93		40·84		39·88
$C^{42}H^{24}O^{20}$ + 4aq.	472	100·00	100·00		100·00		100·00		10·000

Crystallised phlorizin dissolves in 833 pts. *water* at 22° (De Koninck) in 1016 pts. cold water (Boullier). It dissolves very abundantly in

water of 50°, and in all proportions in boiling water (De Koninck). The solubility is not perceptibly increased by addition of dilute acids (Boullier).

With Ammonia. — Crystallised phlorizin absorbs 10 to 12 p. c. ammonia-gas, melting at the same time and solidifying to a colourless mass, which is unalterable in dry air, but in contact with moist air forms phlorizeïn-ammonia (Stas).—Phlorizin dissolves easily in aqueous ammonia, and is precipitated by acids (De Koninck). From the solution, which turns yellow in 24 hours, no phlorizin can afterwards be separated (Boullier).

Phlorizin dissolves easily in aqueous *potash* and *soda*, forming a pale yellow solution, which does not decompose if kept from contact with the air, and still yields phlorizin with acids, even after standing for eight months (Stas).

Barium-compound. — A solution of phlorizin in wood-spirit is precipitated by baryta also dissolved in wood-spirit, the precipitate is washed with wood-spirit, then pressed, and dried out of contact with the air. When thus prepared, it retains a small quantity of wood-spirit, and contains, on the average, 30·01 p. c. BaO; the organic substance exhibits the composition of dried phlorizin (Stas). $2C^{42}H^{24}O^{20}$, 5BaO = 30·45 p. c. BaO.

Strontia also unites with phlorizin.

Calcium-compound. — When phlorizin is added to milk of lime, the lime dissolves through the medium of the phlorizin. On evaporating the solution in vacuo, there remains a yellow mass, containing, on the average, 15·03 p. c. lime (Stas). Therefore $C^{42}H^{24}O^{20}$,HO,3CaO, calc. 15·85 p. c. CaO. (Liebig.)

Lead-compound. — Aqueous phlorizin is precipitated by basic acetate of lead, but not by the neutral acetate (De Koninck). From a mixture of phlorizin and oxide of lead heated to 140°, unaltered phlorizin may be separated by hydrosulphuric acid (Mulder). When basic acetate of lead is poured into aqueous phlorizin, so that a large quantity of the latter may remain in excess, and the precipitate is washed and dried, it contains from 59 to 60 per cent. PbO; but at lower temperatures, precipitates are formed, containing between 55 and 60 per cent. of lead-oxide. The pale yellow precipitate even when dried at 140° in vacuo or in a stream of dry air, still retains water, which does not go off completely below 170°, at which temperature the residue exhibits a deep yellow colour, and contains, on the average, 24·81 p. c. C., 2·13 H., 59·82 PbO., and 13·24 O. (Stas.) Mulder found 62·13 p. c. PbO.

Aqueous phlorizin is not altered by *ferrous* sulphate. With *ferric sulphate*, it forms a yellow-brown precipitate; with ferric chloride it forms a dark brown-red liquid, but no precipitate (De Koninck). The colour disappears on addition of ammonia (Mulder). The aqueous solution of the calcium-compound of phlorizin dissolves *cupric hydrate* (Stas). *Mercuric chloride* and *nitrate of silver* do not alter aqueous phlorizin (De Koninck).

Phlorizin dissolves easily at all temperatures in *wood-spirit* and in *alcohol* (De Koninck, Stas), in 2 pts. alcohol it forms a frothy liquid. (Boullier.) Water precipitates the aqueous solution. Phlorizin dis-

solves very easily in strong *acetic acid*, and is precipitated therefrom by alkalis (De Koninck). — It dissolves very sparingly in *ether* whether cold or at the boiling heat, but easily in *ether-alcohol* (Stas). It is not precipitated from its aqueous solution by *gelatin* (De Koninck).

Phlorizeïn.

$$C^{42}N^2H^{30}O^{26} ?$$
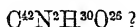
STAS. *Ann. Chim. Phys.* 69, 393 ; *Ann. Pharm.* 30, 206.

Produced when the compound of phlorizin with ammonia is exposed to the air in the moist state, till it acquires a dark blue colour (Stas).

$$C^{42}H^{24}O^{20} + 2NH^3 + 6O = C^{42}N^2H^{30}O^{26} \text{ (Strecker)}.$$
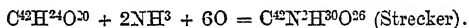
As this reaction must be attended with elimination of water, Weltzien (*Organ. Verb* Braunschweig, 1860, 493) supposes that phlorizeïn contains 4 at. water. The behaviour of phlorizin to ammonia (p. 15) renders it doubtful whether phlorizeïn still contains the radical of glucose (Hlasiwetz, *Ann. Pharm.* 119, 210). See also the reaction of phloroglucin with ammonia in contact with the air (xv, 67), in which similarly coloured bodies are formed.

A number of capsules covered at the bottom with a thin layer of moist phlorizin, are placed above a dish containing a dissolved ammonia-salt; lumps of potash are thrown into this solution, and the whole is covered with a glass bell-jar, the edge of which dips into water, so that the air in the interior is kept moist. After 4 or 5 days, the liquid being stirred and fresh lumps of potash thrown in every day, the phlorizin is converted into a thick, nearly black, syrup, which, besides phlorizeïn, likewise contains phlorizin either unaltered or combined with ammonia, and, especially on the edges of the capsules, a brown-red bitter substance resulting from the decomposition having gone too far; this must at once be carefully removed, as it could not be separated afterwards. The remainder of the product is placed in vacuo over oil of vitriol, to expel the excess of ammonia, then suspended in a little water, and dissolved in a large quantity of alcohol, which dissolves phlorizin and an extractive substance, and separates a precipitate of a fine blue colour. The latter is washed with alcohol, pressed between paper, and well-boiled with alcohol to remove foreign matters. On dissolving the phlorizeïn-ammonia thus obtained in the smallest possible quantity of water, and mixing it by drops with alcohol, acidulated with acetic acid (carefully avoiding an excess of the latter), phlorizeïn separates, and may be washed with strong alcohol.

Properties. Solid, amorphous body like a red resin in the mass, and having a shining fracture. In splinters it is transparent, with red colour. In powder it resembles orceïn. Has a slightly bitter taste. Not fusible.

					Stas. mean.
42 C		252	48·65		48·3
2 N		28	5·40		5·2
30 H		30	5·79		5·7
26 O		208	40·16		40·8
$C^{42}N^2H^{30}O^{26}$		518	100·00		100·00

Stas proposed the formula $C^{64}N^3H^{45}O^{42}$. Strecker (*Ann. Pharm.* 74, 187), the one above given.

Decompositions. 1. Phlorizeïn decomposes when *heated*, without melting or volatilising.—It is instantly decomposed by *chlorine.* In contact with *alkalis* and *air*, it loses its red colour, and is converted into a brown substance.

It dissolves in boiling *water* with red colour, less easily in cold water.

Phlorizeïn-ammonia. — The blue substance obtained as above. — If it be dissolved in a small quantity of ammonia, after being washed with alcohol, and the solution evaporated under a glass jar in the neighbourhood of sticks of potash, it remains in the form of a solid amorphous purple blue substance, with coppery reflex, having a bitter ammoniacal taste, and unalterable in dry air,—gives off ammonia and water when heated. — It is instantly decolorised by chlorine. Strong acids, with the exception of nitric acid, dissolve the compound with blood-red colour, alkalis separate ammonia from the solutions, without destroying the colour. The easily formed, splendid blue solution of the compound in water, gives off ammonia when heated, and deposits red phlorizeïn; likewise on addition of dilute acids. It is instantly decolorised by hydrosulphuric acid, hydrosulphate of ammonia, or staunite of potash, but turns blue again on exposure to the air.— Contains from 44·66 to 45·45 p. c. C., 6·26 H., 6.50 N., and oxygen. Liebig (*Ann. Pharm.* 30, 222) gave the formula $C^{42}N^2H^{29}O^{26},NH^4O$, which, according to Strecker's formulæ, should contain 1 at. hydrogen more (= $C^{12}N^3H^{34}O^{27}$), and would then require 46·32 p.c. C., 7·72 N. and 6·25 H.

Hydrate of alumina immersed in aqueous phlorizeïn-ammonia, turns blue, decolorises the liquid, and sets ammonia free.

Lead-compound of Phlorizeïn. — From the ammonia-compound, basic acetate of lead throws down a precipitate, which, after drying in vacuo, contains on the average, 30·71 p. c. lead-oxide (Stas), answering, according to Strecker, to the formula $C^{42}N^2H^{28}O^{24},2PbO$ (calc. 30·9 p. c. PbO).

Aqueous phlorizeïn-ammonia precipitates *zinc-* and *iron salts.*

Silver-compound. — Thrown down from the ammonia-compound by nitrate of silver, as a blue precipitate, which is decomposed by washing with water, and when dried, after being pressed, at mean temperature, exhibits a pitch-black colour. When thus prepared, it contains from 36·89 to 37·57 p. c. C., 3·9 to 4·4 H., 4·25 N., and 21·66 to 22·75 Ag. (Stas.)

Phlorizeïn scarcely colours *wood spirit, alcohol,* or *ether.*

Æsculin.

$$C^{42}H^{24}O^{26} = C^{18}H^4O^6, 2C^{12}H^{10}O^{10}.$$
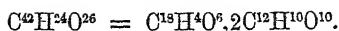
MINOR (1831). *Br. Arch.* 38, 130; *Berz. Jahresber.* 16, 274.
KALBRUNER, *Repert.* 44, 211.
J. B. TROMMSDORFF. *Ann. Pharm.* 14, 189; *Berz. Jahresber.* 16, 283,
ROCHLEDER & SCHWARTZ. *Wien. Akad. Ber.* 10, 70; *Ann. Pharm.* 87. 186; *J. pr. Chem.* 59, 193; abstr. *Pharm. Centr.* 1853, 305; *N. J, Pharm.* 23, 474; *N. Ann. Chim. Phys.* 38, 373; *Chem. Gaz.* 1853. 301.—*Wien. Akad. Ber.* 11, 334; *J. pr. Chem.* 60, 291; abstr. *Ann. Pharm.* 88, 356; *Pharm. Centr.* 1853, 728.
ZWENGER. *Ann. Pharm.* 90, 63; *Pharm. Centr.* 1854, 489; *J. pr. Chem.* 62, 282; *Chem. Gaz.* 1854, 301.
ROCHLEDER. *Wien. Akad. Ber.* 13, 169; *J. pr. Chem.* 64. 29; *Pharm. Centr.* 1854, 722.—*Wien. Akad. Ber.* 16, 1; *J. pr. Chem.* 66, 208. —*Wien. Akad. Ber.* 20, 351; *J. pr. Chem.* 69, 211; *Chem. Centr.* 1856, 869.—*Wien. Akad. Ber.* 23, 1; *J. pr. Chem.* 71, 414; *Chem. Centr.* 1857, 358.—*Wien. Akad. Ber.* 24, 32.

Schillerstoff (Raab); *Bicolorin* (Martius); *Polychrom* (Kastner). *Esculine.*— Frischmann (*Crell. Chem. J.* 5, 5) observed that the infusion of horse-chestnut bark is iridescent; Remmler (*Taschenb.* 1785. 124) endeavoured to isolate the iridescent principle, and appears to have obtained tolerably pure œsculin. Subsequently æsculin was regarded as a salifiable base, or its separate identity was doubted, till Raab (*Kastn. Arch.* 10, 121) discovered it anew, and Minor obtained it in the pure state. — On Fremy's *acide esculique*, see xvi.

Sources. In the bark of the horse-chestnut *Aesculus Hippocastanum* (*Handbuch,* viii. *Phytochemie,* 25.) Most abundantly in March, before the opening of the buds (Jonas).—In *Tamarix gallica* (*ibid* 35), especially in the fresh flowers (Landerer, *Repert.* 33, 377; 84, 72). Whether the fluorescence observed by Loseke (*Mat. med.* 162) in the infusion of privet by Frischmann in that of logwood, and by Nolde (*Crell. Chem. J.* 5, 5) in that of red sandal-wood and of quassia-wood, is due to the presence of æsculin, is a point not yet investigated. Similar remarks apply to the fluorescent substance, which, according to Brandis (*Br. Arch.* 38, 130) exists in angelica root, and in *Semen Stramonii,* and according to Richter (*J. pr. Chem.* 11, 30), in *Radix Belladonnæ.*—The fluorescent principle of the bark of *Fraxinus ornus* (*Handbuch,* viii., *Phytochem.* 48) appears to be fraxin.

¶ According to G. G. Stokes (*Chem. Soc. Qu. J.* 11, 17), the barks of the various species of *Aesculus* and *Pavia* contain two fluorescent substances, viz., æsculin, which exhibits a sky-blue, and paviin, which exhibits a blue-green fluorescence; the former predominates in *Aesculus,* the latter in *Pavia.* Paviin bears a very close resemblance to æsculin, but is distinguished from it by much greater solubility in ether.¶

Preparation. — Ten pounds of pulverised horse-chestnut bark is digested with six times the quantity of alcohol of 80 p. c., the liquid boiled up and filtered hot, and the residue again treated with half the quantity of alcohol. After $\frac{7}{8}$ of the alcohol has been distilled off from the tinctures, the residue is left to itself for some weeks in an open

dish; it then deposits impure æsculin. This crude product, after being freed by ice-cold water from adhering colouring, and pulverulent particles, and from extractive matter, is repeatedly dissolved in the smallest possible quantity of alcohol containing ether, whence it separates on cooling; it is then pressed between bibulous paper. The purification is repeated till the æsculin appears snow-white, and burns without leaving a trace of ash.—All the waste-liquid obtained in the process, together with the waters with which the paper has been washed, are precipitated with solution of glue or isinglass. The precipitate containing tannin is repeatedly kneaded with hot alcohol, and the liquids thus obtained are concentrated, a fresh quantity of æsculin then crystallising out. By this treatment 1lb. of the bark yields 3 drams of æsculin (Trommsdorff). A similar method is pursued by Kalbruner.

2. Comminuted horse-chestnut bark is exhausted with cold water (boiling, according to Rochleder & Schwartz); the infusion is precipitated with neutral acetate of lead; the filtrate is freed from lead by hydrosulphuric acid, and evaporated to a syrup at a moderate heat; and this syrup is left at rest for several days, whereupon it solidifies to a brown mass mixed with white grains. This mass is washed with cold water, and the white grains are collected on a filter. (Minor.)— A similar process is adopted by Rochleder & Schwartz, who further crystallise the product three or four times from weak boiling spirit, and as often from water, and finally wash it with cold water, till $\frac{1}{3}$ of the crystals is dissolved: that which then remains undissolved is pure æsculin.

3. The decoction of horse-chestnut bark is precipitated with solution of alum and a slight excess of ammonia; the cream-coloured precipitate is removed; and the pale wine-yellow filtrate evaporated over the water-bath; it then leaves a residue containing sulphate of potash and ammonia, together with a small quantity of the acetates, and the whole of the æsculin. On boiling this residue with strong alcohol, all the æsculin dissolves out, and may be purified by re-crystallisation from alcohol. This method yields a larger quantity of æsculin than any other. (Rochleder, *Wien. Akad. Ber.* 23, 1.)

4. The aqueous extract prepared by infusion is exhausted with alcohol of 75 p. c.; the tincture is evaporated; the extract dissolved in 6 pts. of alcoholic sal-ammoniac; the clear solution is supersaturated with dilute sulphuric acid, and then again with ammonia, so that it smells strongly of ammonia, and exhibits intense fluorescence. If the proper quantity of ammonia has been added, the liquid becomes turbid immediately, or on being heated, deposits æsculin, an additional quantity of which is obtained by repeated supersaturation with sulphuric acid and ammonia. The mother-liquors are evaporated to two-thirds; a small quantity of gelatin-solution is added, and the precipitate is quickly removed; the filtrate then again yields æsculin. The remainder is obtained by concentrating and extracting with ether containing ammonia. (Jonas, *Ann. Pharm.* 15, 266.)

Properties. Crystallised æsculin (p. 22) contains water, but melts and becomes anhydrous at 160°. After fusion, it solidifies to an amor-

phous fissured mass. Inodorous. Tastes slightly bitter. Colours litmus permanently red. (Zwenger).

Anhydrous.			H. Trommsdorff. mean; at 100°.	Rochleder & Schwartz.	Kawalier.	Zwenger. fused.
42 C	 252	.... 52·07	.... 51·61	.... 51·92	.... 52·11	.... 51·98
24 H	 24	.... 4·96	.... 4·97	.... 5·28	.... 4·99	.... 4·63
26 O	 208	. 42·97	. ... 43·42	.... .. 42·80	.... 42·90	.... 43·39
C⁴²H²⁴O²⁶.. 484		.... 100·00	.... 100 00	... .. 100·00	... 100 00	.... 100·00

Kawalier (*Wien. Akad. Ber.* 16, 1) analysed æsculin dried in a stream of carbonic acid. According to Zwenger, æsculin dried at 100° still retains water; this statement is, however, at variance with the results obtained by other chemists. Rochleder & Schwartz appear to have at first overlooked the water contained in crystallised æsculin; subsequently Rochleder stated that æsculin dried for a day at 100° exhibits the above composition.

Trommsdorff gives the formula $C^{16}H^9O^{10}$; Delffs (*N. Jahrb. Pharm.* 11, 356) gives $C^{22}H^{14}O^{14}$, which latter does not agree with the analysis. Zwenger's formulæ, $C^{76}H^{41}O^{47}$ for fused, and $C^{76}H^{41}O^{47},5HO$ for crystallised æsculin, do not agree with the quantities of sugar found by Rochleder & Schwartz. The above formula is that proposed by Rochleder & Schwartz. More recently (*Wien. Akad. Ber.* 20, 351) Rochleder has given the formula $C^{60}H^{33}O^{37}$ (calc. 54·63 p.c., 5·01 H.) deduced from the quantity of sugar obtained by the decomposition of æsculin.

Decompositions. 1. Æsculin *heated* above its melting point turns yellow or brown. The crystalline mass to which it then solidifies on cooling, contains æsculetin and the decomposition-products of glucose. By dry distillation, crystals of æsculetin are obtained, together with other products. (Zwenger). Dark yellow vapours are given off, which condense to an orange-yellow mass in the neck of the retort; afterwards a little brown empyreumatic oil passes over, whilst a small quantity of gas escapes, and a shining charcoal remains. The distillate dissolves in water to a turbid acid liquid, in which oil and yellow flocks float (Trommsdorff).

2. Æsculin *burnt* on platinum foil emits an odour of caramel, and leaves a carbonaceous residue (Zwenger). In a crucible it melts to a dark brown liquid, which gives off white fumes, smells of caramel, burns with a bright flame, and leaves charcoal (Trommsdorff). — 3. The *aqueous* solution, when kept, loses its fluorescent property, and does not recover it under the influence of alkalis (which colour it blue) (Kalbruner). — 4. Cold dilute *nitric acid* dissolves æsculin, forming a yellow solution, which turns red when supersaturated with potash (Kalbruner). — 5. *Chlorine-water* colours aqueous æsculin red, then brown-red, finally deep yellow, and destroys the fluorescence. On the addition of lime-water, the solution becomes darker and recovers its fluorescent power (Trommsdorff).

6. Æsculin, heated with dilute *sulphuric* or *hydrochloric acid,* is resolved into æsculetin and glucose (Rochleder & Schwartz). Respecting the sugar thus produced, see xv, 341. With acids, Rochleder obtained (from crystallised æsculin? Kr.), from 52·09 to 52·70 p. c. glucose, with emulsin 70·7 p. c. The former statement accords with Rochleder's formula, $C^{60}H^{33}O^{37}$, the decomposition of which, according to the equation $C^{60}H^{33}O^{37} + 3HO = 2C^{18}H^6O^8 + 2C^{12}H^{12}O^{12}$ should yield 54·6 p. c. glucose. According to the formula of Rochleder & Schwartz, $C^{42}H^{24}O^{26} + 6HO = C^{18}H^6O^8 + 2C^{12}H^{12}O^{12}$, dried æsculin should yield 74·3 p. c., crystallised æsculin 70·45 p. c. glucose, agreeing with the second statement. Zwenger's formula $C^{76}H^{41}O^{47} = C^{64}H^{27}O^{33} + C^{12}H^{14}O^{14}$, presupposes the formation of only 21·5 p. c. sugar.

7. By *baryta-water* æsculin is decomposed in the same manner as by acids, but the sugar and æsculetin undergo further alteration, the former being converted into glucic and apoglucic acids, the latter, with assimilation of water, into æsculetic acid (p. 24) (Rochleder).—8. It dissolves in hot aqueous *sesquichloride of iron*, with green colour, due probably to the formation of æsculetin (Rochleder & Schwarz).—9. By continued boiling of æsculin with *cupric oxide* and *potash*, cuprous oxide is formed (Zwenger).—10. A solution of æsculin in cold water, left for some time in contact with *emulsin* at a temperature between 26° and 30°, deposits æsculetin, a small quantity of which remains in solution, together with sugar and emulsin.   100 parts æsculin yield 70·7 pts. glucose dried at 100° (Rochleder & Schwartz).

Combinations. — With *Water.* Æsculin dried at 100°, absorbs only 0·5 to 0·75 p. c. water from the air (Trommsdorff).

A. *Crystallised Æsculin.* Fused amorphous æsculin becomes crystalline when water is poured upon it (Zwenger). Dazzling white slender needles or prisms often grouped in spherules, appearing to the naked eye as a loose powder. From coloured solutions it separates in grains (Trommsdorff).

Crystallised.				Zwenger. at 100°.
42 C	252	49·31		49·45
27 H	27	5·28		5·12
29 O	232	45·41		45·43
$C^{42}H^{24}O^{26}$,3HO . 511		100·00		100·00

B. *Aqueous Solution.* — Æsculin dissolves in 672 pts. water at 10·5°, in 576 pts. at 25°, more abundantly when it contains colouring matter (Trommsdorff), in 300 pts. (Minor). It dissolves in 12·5 pts. boiling water, and the solution solidifies, on cooling, to a loose white pulp, which, when placed upon a filter, allows only one-fourth of the water to drain off. The cold saturated aqueous solution is colourless, and exhibits a faint blue fluorescence, which becomes much stronger on the addition of spring water; 1 pt. of æsculin imparts fluorescence to 1½ million parts of water (Trommsdorff). The solution loses its fluorescence on addition of any acid (according to Kalbruner, boracic acid does not destroy the fluorescence; according to Trommsdorff it does), but recovers it on the addition of alkalis, lime-water or baryta-water (Minor, Trommsdorff, Kalbruner).

Æsculin dissolves in dilute *acids* or *alkalis* more easily than in water; the alkaline solution appears blue by reflected, yellow by transmitted light (Minor). All alkalis colour æsculin yellow, and increase its fluorescence. The solution is sometimes partially decomposed by the alkali, and is then no longer completely decolorised by acids, but leaves on evaporation in vacuo, a brown bitter mass, which dissolves in water, with bright fluorescence (Trommsdorff).

Aqueous æsculin is not precipitated by *metallic salts* (Jonas, Trommsdorff), only by *basic acetate of lead*, forming a yellow precipitate (Minor). The pale yellow precipitate produced by basic acetate of lead is partially decomposed by washing with water or alcohol (Rochleder & Schwartz; Zwenger).

Æsculin does not colour aqueous *iron-salts* (Jonas, vid. sup.).

It dissolves in 120 pts. absolute alcohol; 100 pts. of alcohol of 82 p. c., and in 80 pts. of rectified spirit (Minor); in 24 pts. of boiling alcohol of sp. gr. 0·798 (Trommsdorff).

It is insoluble in *ether* (Minor); nearly insoluble in absolute ether, but somewhat soluble in ether containing water or alcohol, in 17 pts. of a boiling mixture of 1 pt. ether and 5 pts. absolute alcohol (more abundantly then than in pure alcohol ? Gm.); when the solution cools down to 10·5°, 1 pt. of æsculin remains dissolved in 90 pts. of liquid (Trommsdorff).

Appendix to Vol. XIII, p. 345.

Æsculetin.

$$C^{18}H^6O^8 = C^{18}H^6O^6,O^2 ?$$
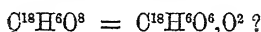
ROCHLEDER & SCHWARTZ. *Wien. Akad. Ber.* 10, 70 ; 11, 334.
ZWENGER. *Ann. Pharm.* 90, 68.
ROCHLEDER. *Wien. Akad. Ber.* 13, 169 ; 20, 351; 24, 32.

The compound produced by the decomposition of æsculin (p. 21).

Preparation. 1. Æsculin is immersed in a quantity of water sufficient to dissolve it on boiling; a quantity of oil of vitrol equal to ⅛ of the volume of the water is added; and the liquid is heated over the water-bath, whereupon the æsculin first dissolves with yellow colour, and the solution afterwards deposits needles of æsculetin. When the evaporation has been carried so far that the liquid begins to blacken on the edges of the basin, it is set aside for 24 hours at 8° to 10°, and the æsculetin is collected and crystallised from boiling water, with help of animal charcoal. The æsculetin thus obtained, which is still slightly yellow, may be rendered white by moistening it with aqueous ammonia, washing it on a filter till ⅓ of it is dissolved, and recrystallising the remainder from boiling water containing hydrochloric acid (Rochleder & Schwarz). — 2. Æsculin is dissolved in warm moderately dilute hydrochloric acid; the liquid is heated for some time to the boiling point, and the crystalline pulp is diluted with cold water, and washed to remove the hydrochloric acid. The nearly pure æsculetin thus obtained is dissolved in warm alcohol, and precipitated with neutral acetate of lead, and the yellow precipitate, after washing with alcohol and with boiling water, is suspended in boiling water, and decomposed by a stream of hydrosulphuric acid gas. The solution filtered from the sulphide of lead at the boiling heat, and left to cool, deposits æsculetin, which may be further purified by recrystallisation (Zwenger). — 3. Æsculin dissolved in cold water is left in contact with emulsin at a temperature of 25° to 30° till æsculetin separates out, and the solution has quite lost the bitter taste of æsculin ; the liquid is then evaporated over the water-bath, and the residue is treated with boiling alcohol, which leaves the emulsin undissolved, and takes up the æsculetin and sugar. The two latter substances are separated by evaporating the alcoholic solution, and treating the residue with cold water, or more completely by precipitating the boiling solution with neutral acetate of lead, filtering, and decomposing the lead-compound of æsculetin with hydrosulphuric acid (Rochleder & Schwartz).

Properties. Crystallised æsculetin (see below) heated to 100° or left over oil of vitriol in vacuo, gives off water, and is converted into anhydrous æsculetin, acquiring a yellowish colour at the same time. Anhydrous æsculetin melts at a temperature above 275° to a yellow-brown oil, which solidifies in the crystalline form, partly volatilising at the same time that it melts. Its taste is bitter and irritating. Neutral. (Zwenger.)

Calculation according to Rochleder & Schwartz.			Zwenger.		
18 C	108	.... 60·67	64 C............ 384	....	60·95
6 H....................	6	.... 3·37	22 H 22	....	3·49
8 O....................	64	.... 35·96	28 O............ 224	....	35·56
$C^{18}H^6O^8$................ 178		.... 100·00	$C^{64}H^{22}O^{28}$.... 630	....	100·00

Rochleder & Schwartz.		Zwenger.
mean; at 100°		*mean; at* 100°.
60·68	....	60·71
3·53	....	3·49
35·79	....	35·80
100·00	....	100·00

The formula of Rochleder & Schwartz is supported by the behaviour of æsculetin to chloride of acetyl, it is also more in accordance with the mode of resolution of æsculin.

Decompositions. 1. Æsculetin, when *heated*, melts, turns brown, chars, and is for the most part decomposed, small quantities of a yellow oil passing over, together with crystals, probably of unaltered æsculetin (Rochleder & Schwartz). — 2. It is decomposed by hot *oil of vitriol* (Zwenger). — 3. By *nitric acid* it is oxidised to oxalic acid (Zwenger). — 4. *Baryta-water* converts æsculetin into æsculetic acid, $C^{18}H^{12}O^{14}$, whose baryta-salt is represented by the formula $C^{18}H^{11}BaO^{14}$, and its lead-salt, by $6C^{18}H^{10}O^{12}$, $10PbO$ (Rochleder). — 5. Æsculetin reduces a boiling *alkaline solution of cupric oxide* to cuprous oxide, *nitrate of silver* to metallic silver, quickly with aid of heat, after considerable time only, in the cold. — 6. Æsculetin dissolves readily in a boiling concentrated aqueous solution of *bisulphite of ammonia*, and does not separate on cooling. The yellowish solution mixed with alkalis, rapidly absorbs oxygen from the air; it is coloured darker by ammonia, and if then shaken up with air, assumes a blood-red, and ultimately a deep indigo-blue colour (baryta-water in place of ammonia, precipitates sulphite of baryta, after removal of which the liquid appears a blood-red), whereupon, baryta or lead-salts throw down a deep violet or dark indigo-blue precipitate according as the liquid has an acid or a neutral reaction. On decomposing the lead-salt with hydrosulphuric acid, a liquid is obtained colourless when dilute, green when concentrated, and acquiring a splendid blood-red colour on exposure to the air. By evaporation, dry distillation, or precipitation of these liquids with bases, red, green, or blue substances are obtained, all containing nitrogen and sulphur, but the nitrogen not in the form of ammonia, and the sulphur neither as sulphurous nor as hydrosulphuric acid (Rochleder). — 7. Æsculetin heated with *chloride of acetyl* containing traces of terchloride of phosphorus, is converted into acetyl-æsculetin. Pure chloride of acetyl appears not to act, at least in similar cases (comp. xiii, 242.)   (Nachbaur.)

Combinations. With *Water.* — A. *Crystallised Æsculetin.* Colourless needles and laminæ, with a silky lustre, like benzoic acid, and forming a silky film when dried on the filter (Rochleder and Schwartz; Zwenger). Æsculetin prepared by the action of emulsin is white; that which is obtained with acids is slightly yellow, and cannot be deprived of its colour (Rochleder).—At 100° or in vacuo, it loses on the average 6·7 p.c. water, and is converted into anhydrous æsculetin (Zwenger).

	a.				*b.*			Zwenger. *air-dried.*
36 C	216	....	56·39	64 C	384	....	56·88	.... 56·67
15 H	15	....	3·92	27 H	27	....	4·00	.... 4·18
19 O	152	....	39·69	33 O	264	....	39·12	.... 39·15
$2C^{18}H^6O^8,3HO$...	383	....	100·00	$C^{64}H^{32}O^{23},5HO$....	675	...	100.00	.... 100·00

Zwenger gives the formula *b*, according to *a*, the calculated amount of water in crystallised æsculetin is 7·65 p.c.; according to *b*, it is 6·6 p.c.

Æsculetin dissolves very slightly in cold, more easily in boiling water. The cold saturated solution is colourless; that which is saturated at the boiling heat is yellowish; both exhibit a faint blue colour by reflected light, becoming stronger on addition of a small quantity of carbonate of ammonia, whereas acids destroy the colour (Zwenger).

Dissolves in fuming *hydrochloric acid,* and crystallises therefrom in large laminæ and needles.

Ammonia-compound. — Colourless æsculetin exposed to air containing ammonia, acquires a flesh colour, like that of hydrated sulphide of manganese (Rochleder). The saturated solution of æsculetin in hot aqueous ammonia deposits on cooling shining lemon-yellow laminæ, which when exposed to the air for a few hours, give off all their ammonia and turn white (Rochleder & Schwartz).

Æsculetin dissolves readily in dilute aqueous *alkalis,* forming a gold-yellow solution, from which it is precipitated by acids in needles. A trace of alkali or of an alkaline earth colours aqueous æsculetin intensely yellow (Rochleder & Schwartz, Zwenger).

Lead-compound. — Neutral acetate of lead precipitates æsculetin, both from its aqueous and from its alcoholic solutions. The precipitate obtained from boiling aqueous æsculetin is light yellow and gelatinous, becomes darker after drying at 100°, and contains 49·34 p. c. lead-oxide (Rochleder and Schwartz), 57·54 p. c. (Zwenger). — An alcoholic solution of neutral acetate of lead added to alcoholic æsculetin forms a precipitate of a fine lemon-yellow colour containing 57·66 p. c. lead-oxide (Rochleder and Schwartz), 57·33 p. c. (Zwenger). — The compound when set on fire, burns with a glimmering light, sometimes with sparkling, dissolves speedily in water when freshly precipitated, easily in acids (Zwenger).

					Rochleder & Schwartz.	Zwenger. *mean.*
18 C	108	....	28·12	....	28·71	.... 28·38
4 H	4	....	1·04	....	1·19	.... 1·22
6 O	48	....	12·50	....	12·44	.... 12·85
2PbO	224	....	58·34	....	57·66	..... 57·55
$C^{18}H^4Pb^2O^8$	384	....	100·00	....	100·00	.... 100·00

Rochleder's salt was obtained from alcoholic, Zwenger's from aqueous solution; the former gives the formula $10C^{18}H^4O^6,19PbO$, the latter $C^{64}H^{15}O^{21},7PbO$. Rochleder & Schwartz likewise analysed a lead-salt precipitated from aqueous solution, which yielded 20·95 p.c. C., 2·17 H., 20·54 O., and 49·34 PbO., whence they deduced the formula $6C^{18}H^8O^{10},11PbO$. Zwenger did not obtain a salt agreeing in amount of lead with this formula.

Aqueous æsculetin is coloured dark green by *ferric* (not by ferrous) salts, without precipitation. The coloured is destroyed by acids.

Æsculetin is slightly soluble in cold, easily in boiling *alcohol*, insoluble in *ether*.

Acetyl-æsculetin.

$$C^{30}H^{12}O^{14} = 3C^4H^3O^3,C^{18}H^3O^5.$$
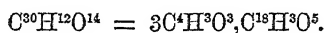
NACHBAUR. *Ann. Pharm.* 107, 248; abstr. *Rép. Chim. pure*, 1, 107.

Æsculetin is heated over the water-bath with chloride of acetyl containing traces of terchloride of phosphorus (p. 24). The mixture boils at first with violent percussion, but gradually yields, with elimination of hydrochloric acid, a solution, the residue of which, after removal of the excess of chloride of acetyl, solidifies in the crystalline form. It may be purified by recrystallisation from boiling water.

Small dazzling needles which dissolve in alcohol and ether, and do not colour sesquichloride of iron.

					Nachbaur.
					mean.
30	C	180	....	59·21	59·06
12	H	12	....	3·95	4·17
14	O	112	....	36·84	36·77
$C^{18}(3C^4H^3O^2)H^3O^8$		304	....	100·00	100·00

Glucosides with 20 at. Carbon in the Copula.

Pinipicrin.

$$C^{44}H^{36}O^{22} = C^{20}H^{16}O^2,2C^{12}H^{10}O^{10}.$$
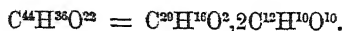
KAWALIER. *Wien. Akad. Ber.* 11, 350; *J. pr. Chem.* 60, 321; abstr. *Ann. Pharm.* 88, 360; *Pharm. Centr.* 1853, 705 and 724.—*Wien. Akad. Ber.* 13, 515; *J. pr. Chem.* 64, 16; *Pharm. Centr.* 1854, 881; *Chem. Gaz.* 1855, 45.

Occurrence.—In the needles, inner bark and outer bark of the Scotch fir, *Pinus sylvestris.* In the green parts of *Thuja occidentalis.*

Preparation.—The comminuted needles of the Scotch fir (or branches of Thuja) are exhausted with alcohol of 40°; the alcohol is distilled off from the decoction, and the residue is mixed with water, which separates a green mass of resin (serving for the preparation of kinovous acid, xv. 33),

while the supernatant turbid liquid retains in solution pinipicrin, sugar, traces of citric acid, oxypinitannic acid, and pinitannic acid. This liquid is mixed with a few drops of neutral acetate of lead, which renders it filtrable; the filtrate is mixed with excess of that reagent, which throws down oxypinitannate of lead; then, after another filtration, pinitannate of lead is precipitated by the basic acetate; this is also separated by filtration after the liquid has cooled; and the filtrate is saturated with hydrosulphuric acid. The liquid, freed from sulphide of lead, and evaporated in a stream of carbonic acid, leaves a residue of the consistence of an extract, from which anhydrous ether-alcohol extracts the pinipicrin and leaves the sugar. A small quantity of the foreign substance is precipitated from the solution by basic acetate of lead; the filtrate is treated with hydrosulphuric acid; the sulphide of lead is removed, and the liquid evaporated. By repeatedly dissolving the residue left after the ether-alcohol has been distilled off, in fresh quantities of anhydrous alcohol containing ether, as long as any insoluble matter is left, and evaporating the solution, pinipicrin is at length obtained, still, however, contaminated with acetic acid, which adheres to it obstinately, but may be removed by agitation with a little pure ether (which, however, at the same time, removes a little pinipicrin). — The needles, after exhaustion with alcohol, still retain a little pinipicrin, which may be obtained from the aqueous decoction in the same manner as from the alcoholic.

Properties. Bright yellow powder, which softens at 55°, becomes viscid at 80°, transparent and mobile at 100°, and solidifies on cooling to a brownish yellow, brittle, friable mass. Hygroscopic. Tastes strongly bitter.

		In vacuo.				Kawalier. *a. mean.*		*b.*
44	C	264	....	55·46	....	55·45	....	55·45
36	H	36	....	7·56	....	7·51	....	7·62
22	O	176	....	36·98	....	37·04	....	36·93
$C^{44}H^{36}O^{22}$		476	.. .	100·00	....	100 00	.. ..	100 00

a. from pine-needles; *b.* from *Thuja.*

Decompositions. 1. Pinipicrin swells up strongly when *heated* on platinum-foil, and leaves a difficultly combustible charcoal. — 2. The aqueous solution, when heated, instantly gives off the odour of ericinol (p. 29), and is completely resolved into this substance and glucose:

$$C^{44}H^{36}O^{22} + 4HO = C^{24}H^{24}O^{24} + C^{20}H^{16}O^{2} \text{ (Kawalier).}$$
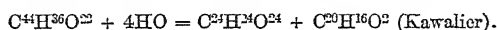
In contact with *emulsin* it emits an odour of volatile oil, but the action soon ceases. (Kawalier, *Wien. Akad. Ber.* 12, 549).

Pinipicrin dissolves readily in *water.* It dissolves in *alcohol,* ether-alcohol, and in aqueous but not in pure *ether.*

Ericolin.

$$? \ C^{68}H^{56}O^{42} = C^{20}H^{16}O^2, 4C^{12}H^{10}O^{10}.$$
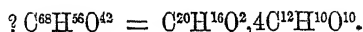
ROCHLEDER & SCHWARTZ.   *Wien. Akad. Ber.* 9, 308; *J. pr. Chem.* 58, 210; *Ann. Pharm.* 84, 366; *Pharm. Centr.* 1852, 212.— *Wien. Akad. Ber.* 11, 371; *Pharm. Centr.* 1853, 861.

Occurrence. In the herb of *Ledum palustre*, less abundantly in that of *Calluna vulgaris, Erica herbacea,* and *Rhododendron ferrugineum.* In the herb of *Arctostaphylos uva ursi,* passing into the mother-liquor of the arbutin (xv, 419). (Kawalier, *Wien. Akad. Ber.* 9, 297.)

Preparation. From *Ledum palustre.* 1. The chopped leaves are thrown into boiling water, and boiled for several hours; the liquid is strained, and precipitated with basic acetate of lead; the filtrate is evaporated in a retort to one-third, and filtered from the separated lead-salt; the liquid freed from lead by hydrosulphuric acid is evaporated to an extract, and from this the ericolin is dissolved out by anhydrous ether-alcohol. The residue left after evaporation of the ether-alcohol is repeatedly taken up by the same solvent till it no longer yields any insoluble residue.— 2. The aqueous decoction of *Ledum palustre* is evaporated to the consistence of honey; this extract is mixed with alcohol of 40° and filtered, the filtrate is precipitated with baryta-water, and the precipitated leditannate of barium is separated. Carbonic acid is then passed into the liquid; neutral and basic acetate of lead, the latter in excess, are successively added; and the whole of the resulting precipitates are collected. The filtrate mixed with alcohol deposits a white lead-salt, which is washed with alcohol and decomposed under water by hydrosulphuric acid, and on filtering the liquid from sulphide of lead, and evaporating in a stream of carbonic acid, ericolin remains behind.

Properties. Brown-yellow powder which cakes together at 100°, and has a very bitter taste.

		at 100°.				Rochleder & Schwartz.
68 C	.....	408	.....	51·00	.....	51·71
56 H	.....	56	.....	7·00	.....	7·19
42 O	.....	336	.....	42·00	.....	41·10
$C^{68}H^{56}O^{42}$	.....	800	.....	100·00	.....	100·00

Contained 10·6 p.c. ash. Rochleder & Schwartz give the formula $C^{68}H^{55}O^{41}$. It is perhaps identical with pinipicrin (p. 26).

Ericolin, heated with dilute sulphuric acid, is resolved into ericinol (p. 29) and sugar:

$$C^{68}H^{56}O^{42} + 8HO = C^{20}H^{16}O^2 + 4C^{12}H^{12}O^{12}.$$

Appendix to XIV, 350.

Ericinol.

$$C^{20}H^{16}O^2 = C^{20}H^{16}_{,}O^2?$$
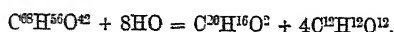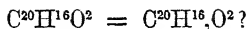
Different from Uloth's *Ericinone* (*Ann. Pharm.* 111, 215), a product from ericaceous plants, analogous to hydrokinone.

Pinipicrin (p. 26) or ericolin (p. 28) boiled with dilute acids, yields, together with sugar, a partially altered oil, which, according to Kawalier, and Rochleder & Schwartz, consists of ericinol, a copula of these glucosides. The same volatile oil, but likewise in an altered state, is obtained from *Calluna vulgaris*, and *Rhododendron ferrugineum*, according to Rochleder; from *Arctostaphylos uva ursi*, according to Kawalier, from *Ledum palustre*, according to Willigk; and from *Erica herbacea* according to Kuberth (Rochleder & Schwarz). It is a constituent of the volatile oil of *Ledum palustre*. (Fröhde.)

1. The oil obtained by heating ericolin with dilute acids, is colourless, absorbs oxygen rapidly from the air, becoming dark-brown, and then contains 68·15 p. c. C., 9·37 H., and 22·48 O., agreeing with the formula $C^{20}H^{16}O^5$ or $C^{20}H^{16}O^2 + 3$ O (calc. 68·18 C., 9·09 H., 22·73 O.) (Kawalier, *Wien. Akad. Ber.* 9, 297). When the aqueous decoction of *Ledum* is precipitated with neutral and basic acetate of lead, and the filtrate, after being freed from lead, is distilled with dilute sulphuric acid, a resin separates out, while a volatile oil passes over, and carbonic acid is set free. The volatile oil contains 79·08 p. c. carbon, 10·33 hydrogen, and 10·59 oxygen, is therefore $C^{20}H^{15}O^2$ (calc. 79·47 p. c. C., 9·93 H., and 10·60 O.), and is produced from ericolin (E. Willigk, *Wien. Akad. Ber.* 9, 305). — 2. When aqueous pinipicrin is distilled with dilute sulphuric acid, a volatile oil passes over, which turns brown when dehydrated in a half-filled vessel, and then contains 73·66 p. c. C., 9·66 H., and 16·68 O., and is therefore $C^{60}H^{48}O^{10}$ (calc. 73·77 C., 9·84 H., and 16·39 O.) or $3C^{20}H^{16}O^2 + 4$ O. In the residue there remains a resin, likewise produced by oxidation of ericinol. (Kawalier, *Wien. Akad. Ber.* 11, 350). — 3. The leaves of *Rhododendron ferrugineum* (*Handbuch*, viii. *Phytochem.* 64) yield by distillation, a pale yellow, volatile oil, which, when distilled over anhydrous phosphoric acid becomes colourless, and acquires the odour of oil of turpentine. (R. Schwartz, *Wien. Akad. Ber.* 9, 301.)

	a.		Schwartz.		*b.*		Schwartz.
80 C	84·51	....	84·19	80 C	85·71	....	85·85
64 H	11·26	....	11·22	64 H	11·43	....	11·73
3 O	4·23	....	4·59	2 O	2·86	....	2·42
$C^{80}H^{64}O^3$	100·00	....	100·00	$C^{80}H^{64}O^2$	100·00	....	100·00

a. and *b.* were from different preparations.

4. By distilling *Ledum palustre* with water, a pale yellow oil is likewise obtained, containing 82·35 p. c. C., 10·89 H., and 6·76 O., identical with the oil produced from ericolin, and agreeing with the formula $C^{80}H^{68}O^5$ (calc. 82·33 p. c. C., 10·80 H., and 6·87 O.) (Willigk.)

5. The volatile oil of *Ledum palustre (Handbuch, loc. cit.)* obtained by distilling the herb with water, is a mixture containing valerianic acid and other volatile acids, an oily acid $C^{16}H^{10}O^8$, an oil isomeric with oil of turpentine, boiling at 160°, and ericinol. When freed from the acids by repeated agitation with strong potash-ley, then washed and dehydrated, it gives off between 115° and 160°, a mixture of non-oxygenated oil and ericinol, between 236° and 250°, chiefly ericinol, and leaves a resin.

This ericinol, which boils between 240° and 242°, is blue-green, has an unpleasant odour, and a burning, nauseously bitter taste. By one distillation with sticks of potash, it is partially decolorised, and then exhibits a specific gravity of 0·874 at 20° C., and a composition corresponding with the formula $C^{20}H^{16}O^2$. By cohobation[1] with excess of potash-hydrate, it is converted into a non-oxygenated oil, $C^{20}H^{16}$ (Fröhde, *J. pr. Chem.* 82, 181).

					Fröhde.
20 C	120	78·96	79·85	80·07
16 H	16	10·52	11·02	11·05
2 O	16	10·52	9·13	8·88
$C^{20}H^{16}O^2$	152	100·00	100·00	100·00

Willigk's analysis also nearly agrees with this formula (see page 29).

Menyanthin.

LUDWIG & KROMAYER. *N. Br. Arch.* 108, 263; *Analyt. Zeitschr.* 1, 15. KROMAYER, *Die Bitterstoffe.* Erlangen, 1861, p. 28.

R. Brandes (*Mag. Pharm.* 33, 271. — *N. Br. Arch.* 30, 154; *Jahrb. pr. Pharm.* 2, 284), endeavoured to separate the bitter principle of the common buckbean (*Menyanthes trifoliata*), and obtained it in the form of a yellow extract, but impure. On Landerer's bitter crystals from the ethereal extract of buckbean, see *Repert.* 68, 65.

Preparation. 1. Buckbean is repeatedly exhausted with hot water, and the infusion concentrated and shaken up with animal charcoal, which takes up the menyanthin. The charcoal is washed with cold water, and boiled with alcohol; the alcohol is distilled from the tincture, the residue diluted with water, and precipitated with basic acetate of lead, and the filtrate is freed from lead by hydrosulphuric acid. From the filtrate neutralised with carbonate of lime, the menyanthin is again precipitated by bone charcoal, and (after the charcoal has been washed with cold water) it is again extracted by boiling alcohol. The crude menyanthin obtained by evaporating the alcholic solution is precipitated from the aqueous solution by tannic acid, and the washed precipitate is decomposed by digestion with alcohol and levigated litharge. The mixture is evaporated to dryness over the water-bath, the residue is well boiled with alcohol, and the alcoholic solution is evaporated. After the greater part of the alcohol has evaporated, oily drops separate out, which must be treated with ether, to free them from an irritating substance, and dried in vacuo, over oil of vitriol.—2. Buckbean is repeatedly exhausted with hot water; the extracts, after being clarified and concentrated, are precipitated with infusion of galls; the

precipitate is washed, mixed with levigated oxide of lead, dried over the water-bath, and boiled with alcohol of 85 per cent. The alcohol is distilled off, and the filtered residue left to evaporate slowly, whereupon menyanthin is separated as a brownish mass having the consistence of turpentine. This is washed repeatedly with water and ether in succession; the residue is dissolved in hot water; the solution precipitated after cooling with aqueous tannic acid; the plaster-like precipitate is washed, and again decomposed in alcoholic solution with oxide of lead; the solution evaporated to dryness; the residue boiled with alcohol; and the liquid, after being decolorised with animal charcoal and diluted with water, is left to evaporate; it then deposits menyanthin as a colourless turpentine-like mass, which solidifies when dried over oil of vitriol.

Properties. Amorphous, nearly white friable mass. Softens at $60°$-$65°$, becomes transparent at $75°$, tough at $100°$, mobile at $115°$, and solidifies to a hard, yellow, transparent mass. Tastes strongly and purely bitter. Permanent in the air. Neutral.

Calculation according to Ludwig & Kromayer.				Ludwig & Kromayer.
44 C	264	55·46		55·68
36 H	36	7·56		7·67
22 O	176	36·98		36·65
$C^{44}H^{36}O^{22}$	476	100·00		100·00

Or perhaps $C^{66}H^{54}O^{32}$. Isomeric with and related to pinipicrin p. 26. (Ludwig & Kromayer.)

Decompositions. 1. Menyanthin melts on platinum-foil, emitting an aromatic odour and acrid biting vapours, and *burns away* without residue. — 2. It dissolves in *oil of vitriol*, forming a yellow-brown liquid, which becomes violet-red on standing, and deposits grey flocks when mixed with water. — 3. Aqueous menyanthin heated with *dilute sulphuric acid*, is resolved into a volatile oil and a fermentable sugar. The quantity of the latter amounts to 22·26 p. c. of the menyanthin. A brown resin formed at the same time appears to be an intermediate substance produced by the decomposition of the volatile oil. — The volatile oil resulting from the resolution of the menyanthin, Ludwig & Kromayer's *menyanthol*, is colourless, heavier than water, smells like bitter almonds, and is slightly acid. It reduces an ammoniacal solution of silver.

Menyanthin dissolves sparingly in cold, easily in boiling *water*, the solution saturated at the boiling heat becomes milky on cooling. Menyanthin dissolves without alteration in aqueous *alkalis*, and is not precipitated from aqueous solution by metallic salts.

It dissolves in *alcohol*, but not in *ether.*

Tannate of Menyanthin. — From an aqueous solution of menyanthin, aqueous tannic acid throws down a white precipitate, which cakes together to a plaster, and dries up to a grey friable mass. Tastes bitter and astringent. Dissolves readily in alcohol, gives off 3·29 p. c. water at $100°$, and then contains 52·77 p. c. C., 5·89 H., and 41·34 O, whence Ludwig calculates the formula $C^{44}H^{34}O^{22} + 2C^{18}H^{8}O^{12}$ (tannic acid, according to Ludwig), and in another place, the formula, $C^{66}H^{54}O^{34},3C^{18}H^{8}O^{12}$.

Second Body from Buckbean.

When the decoction of buckbean, after precipitation with infusion of galls, and separation of the tannate of menyanthin by filtration, is mixed with lead-oxide and evaporated to a syrup, and the latter is exhausted with ether, the ether takes up a substance, which, after evaporation of the ether, remains as a slightly acid, brown, viscid oil, having an irritating bitter taste, and not volatile with vapour of water.

It reduces *nitrate of silver*. — Decomposes when its aqueous solution is boiled with dilute sulphuric acid, depositing a small quantity of resin, and giving off a heavy, acid, volatile oil, having an aromatic odour (but not that of bitter almonds). No sugar is formed in this reaction.

This substance is insoluble in cold water, but dissolves in *hot water*, and in *aqueous alkalis*. It is precipitated by *basic acetate of lead*, but not by gallo-tannic acid. It is soluble in *alcohol*. (Kromayer, *Die Bitterstoffe*. Erlangen 1861, 30.)

Rubian.

$$C^{56}H^{34}O^{30}.$$
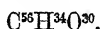
ED. SCHUNCK (1847). 1. In detail: *Ann. Pharm.* 66, 174; abstr. *Pharm. Centr.* 1848, 609 and 625; *Compt. chim.* 1849, 215. — Simultaneously, and in part with different (and incorrect) statements: *Phil. Mag. J.* 33, 133; *J. pr. Chem.* 45, 286. — In part, and with some new statements: *Phil. Mag. J.* 35, 204; *J. pr. Chem.* 48, 299; abstr. *Pharm. Centr.* 1850, 161. — Preliminary Notice of the results: *Phil. Mag. J.* 31, 46; *J. pr. Chem.* 42, 13; abstr. *Pharm. Centr.* 1847, 702.

2. *N. Phil. Mag. J.* 3, 213 and 354; in part *J. pr. Chem.* 55, 490; abstr. *Ann. Pharm.* 81, 336; *Pharm. Centr.* 1852, 305; *N. Ann. Chim. Phys.* 55, 366. — Preliminary Notice: *N. Phil. Mag. J.* 1, 425; *Chem. Gaz*, 1851, 117; *Instit.* 1851, 247.

3. *N. Phil. Mag. J.* 5, 410 and 495; *J pr. Chem.* 59, 453; abstr. *Ann. Pharm.* 87, 344. — Preliminary Notice: *N. Phil. Mag. J.* 4, 472; *Chem. Gaz.* 1852, 436; *Instit.* 1853, 69.

4. *N. Phil. Mag. J.* 12, 200 and 270; *J. pr. Chem.* 70, 154. — Preliminary Notice: *Chem. Gaz.* 1855, 357; *J. pr. Chem.* 67, 154; abstr. *Pharm. Centr.* 1855, 785.

5. *Chem. Soc. Qu. J.* 12, 198; abstr. *Zeitschr. Ch. Pharm.* 3, 67 and 158.

See also: LAURENT, against SCHUNCK's formulæ: *N. Ann. Chim. Phys.* 36, 322; SCHUNCK's reply: *N. Phil Mag. J.* 6, 187; *J. pr. Chem.* 61, 65; DEBUS against SCHUNCK: *Ann. Pharm.* 86, 117; *N. Ann. Chim. Phys.* 38, 490; lastly, GERHARDT, *Traité* 3, 489.

Occurrence. In the root of madder (*Rubia tinctorum*).

Besides purpurin, already described at page 325, vol. xiii, and alizarin, at page 129, vol. xiv, the following substances may be either directly separated from madder, or obtained by decomposition of substances contained in it.

a. Glucosides, yielding by their decomposition, alizarin (sometimes together with many other bodies) and introduced here on that account.
Rubian.   Rubihydran.   Rubidehydran.
Rubianic acid.   Ruberythric acid.   Chlororubian.

b. Substances arising from the decomposition of the glucosides, and in part existing ready formed in the madder.
α. Produced for the most part from rubian.
Rubiacin.   Rubiretin.   Verantin.
Rubiacic acid.   Rubiadin.   Rubiafin.
Rubiagin.   Rubianin.   Rubiadipin.
β. Produced from chlororubian.   •
Oxyrubian.   Perchlororubian.   Chlorubiadin.

c. Rubichloric acid, a compound allied to the tannic acids, and perhaps identical with chlorogenin; its decomposition-product chlororubin; the ferment of madder, erythrozym; and, lastly, the xanthin of Higgin, and that off Kuhlmann, both apparently of mixed nature.

It will be better to describe all these madder-substances together, than to scatter them through the Handbook, on account of their formulæ, which in some instances are but imperfectly established, and for the most part are not in accordance with the fundamental principles of the work (Kr.).

Preparation of Rubian. 1. Coarsely pulverised madder-root (Schunck uses it after it has been gathered for some weeks) is well boiled with water (1lb. of the root to 16 quarts of water); the liquid, after several hours' boiling, is strained through calico (the residue exhausted with water, still contains alizarin and rubiacin, to be separated by the method described under alizarin, xiv. 133); and the liquid is precipitated with dilute sulphuric (or hydrochloric) acid. A dark brown precipitate is thus obtained, which, when separated by decantation and filtration, and freed from excess of acid by washing with a quatity of cold water just sufficient for the purpose (a larger quantity dissolves rubiacin), contains seven substances, viz., rubian, alizarin, rubiacin, rubiretin, verantin, pectic acid, and a dark brown product of the decomposition of extractive matters. The filtrate retains chlorogenin and a small quantity of sugar. The precipitate, while still moist, is boiled with alcohol, as long as the alcohol acquires a yellow colour, and the liquid is filtered hot. In the residue there remains pectic acid, and oxidised extractive matter. The dark brown decoction, on cooling, frequently deposits verantin as a dark-brown resinous powder, which must be separated by filtration. The alcoholic solution, after being again heated to the boiling point, is mixed and digested with recently precipitated hydrate of alumina till the solution is nearly decolorised, whereby alizarin, rubian, rubiacin, and part of the rubiretin and verantin are precipitated, while another portion of the two last-mentioned substances remains dissolved in the alcohol.

α. *Separation of Alizarin.* The alumina-precipitate after being washed with alcohol, is added to a concentrated boiling solution of carbonate of potash; the deep red solution, containing all the other substances is filtered from the undissolved compound of alizarin and alumina; this substance is repeatedly boiled with aqueous carbonate of potash, till the liquid, which runs off on filtration, exhibits only a faint purple colour; and the residue is decomposed by boiling hydrochloric acid, for the preparation of alizarin as described at page 133, vol. xiv.

β. Of Rubian. The deep red alkaline liquid filtered from the compound of alizarin and alumina, still retains in solution, rubian, rubiacin, rubiretin and verantin, which may all be precipitated by hydrochloric acid, then collected and washed with cold water, till the liquid which runs off is free from acid. As soon as this point is attained, the rubian, which is insoluble in acidulated water, begins to dissolve in the pure water, imparting to that which runs off a yellow colour and bitter taste, so that at length it is completely dissolved, and may be obtained as a yellow extract by evaporating the filtrate. It still, however, retains pectic acid, which remains behind on dissolving the extract in alcohol, and from 5 to 8 p. c. ash, from which it cannot be separated.

γ. Of Rubiacin, Rubiretin and Verantin. The residue left after the rubian has been washed out, is mixed with that which remains on evaporating the alcoholic liquid above-mentioned, containing verantin and rubiretin, and the mixture is treated with a boiling solution of ferric chloride or nitrate. Rubiretin and rubiacin then dissolve (the latter partly as such, partly converted, with assumption of oxygen, into ferric rubiacate), while verantin remains behind in combination with ferric oxide. The deep red-brown solution is filtered after boiling for some time; the residue is kept for the preparation of verantin, the rubiacin, rubiacic acid and rubiretin are thrown down from the filtrate as a yellow precipitate, turning brown during washing; and this precipitate, while still moist, is dissolved in boiling alcohol, which takes up the rubiacin and rubiretin, and deposits the former, on cooling, in small lemon-yellow crystals. (The rubiacic acid which remains in solution is purified in the manner described below,—the crystallised rubiacin by converting it into rubiacic acid, from which it may be again obtained as rubiacin). By further evaporation of the alcohol, a mixture of rubiacin and rubiretin is obtained as a dark brown-red residue, which, when boiled with water, deposits dark brown drops of rubiretin, whilst rubiacin remains suspended as a light powder, and and may be removed by decantation. After boiling several times with water, as long as any yellow powder remains, and then decanting, rubiretin ultimately remains in the form of a dark red-brown mass.

2. One pound of Avignon madder is exhausted on a cloth strainer by pouring four or five quarts of boiling water upon it; the dark, yellowish brown, still hot filtrate, is mixed with an ounce of bone-charcoal, stirred, and left to settle; the still brown liquid is decanted; and the residue is collected and washed with cold water, till the liquid which runs off becomes green when boiled with hydrochloric acid (from the presence of chlorogenin). The washed bone-charcoal, if boiled with alcohol, as long as it colours the liquid yellow, yields to it the rubian which it has carried down, and on evaporating the alcoholic solution, the rubian is left behind, but still impure, containing chlorogenin. To remove the latter, the impure rubian obtained in the manner just described is again precipitated in the same manner on the previously used charcoal, which now takes up only the rubian (no chlorogenin), and again extracted by boiling alcohol, the series of operations being repeated a third time with the same bone-charcoal, in case the alcoholic solution still contains chlorogenin. As fresh bone-charcoal precipitates both rubian and chlorogenin, and whereas charcoal, which has once been used for this purpose and boiled out with alcohol, precipitates only the former, or at least gives up only the former to boiling alcohol, it is best not to extract, for the purpose of purification, the first portion of rubian taken up by fresh

bone-charcoal, but to use this charcoal for the preparation of purer rubian On evaporating the alcoholic solutions, the rubian remains behind, still retaining a small quantity of a decomposition-product formed by the action of heat. This is separated, either: *a.* By evaporating the greater part of the alcohol, mixing the solution when cold with dilute sulphuric acid (which throws down the decomposition-product in brown resinous drops), removing the sulphuric acid by carbonate of lead, then filtering, and, evaporating over the water-bath; or *b.* By precipitating the solution with neutral acetate of lead; filtering from the brown-red flocks which separate, and adding basic acetate of lead, whereby a compound of rubian with lead-oxide is precipitated, which must be washed with alcohol, and decomposed by hydrosulphuric or dilute sulphuric acid. In the latter case the excess of sulphuric acid must be removed, as in *a.*—1 cwt. of madder yields 1000 grammes of rubian.

Properties. Hard, dry, brittle, perfectly amorphous mass, resembling dried varnish or gum-arabic, not at all deliquescent, transparent and deep yellow in thin layers, dark brown in thicker masses. Has an intensely bitter taste.

Calculation according to Schunck.				Schunck.
56 C 336	.. ..	55·08	....	54·85
34 H 34	....	5·57	. ....	5·57
30 O 240	....	39·35	... .	39·58
$C^{56}H^{34}O^{30}$ 610	....	100·00	....	100·00

Calculated to 100 pts. after deduction of 5·23 to 7·65 p.c. ash, consisting for the most part of carbonate of lime (Schunck), Rochleder regards rubian as impure ruberythric acid; whereas Schunck considers the latter as a product of the decomposition of rubian: he also regards as decomposition-products of rubian and chlorogenin the following substances:—the xanthin of Kuhlmann, the xanthin of Higgin, and the madder-yellow of Runge (see below).

Gerhardt suggested for rubian the formula $C^{32}H^{16}O^{16}$,Aq. (calc. 55·81 p.c. C., 4·94 H., and 39·25 O.), according to which, the formation of alizarin and glucose would be represented by the equation, $C^{32}H^{16}O^{16}$,2HO = $C^{20}H^6O^6$ + $C^{12}H^{12}O^{12}$; but this formula does not explain the formation of rubianic acid from rubian.

Decompositions. 1. Rubian *heated* in a test-tube decomposes and gives off water at 130°; at a higher temperature, it emits orange-coloured vapours, chiefly consisting of alizarin, and leaves much charcoal. — 2. Heated on platinum foil, it melts, swells up, *burns* with flame, and leaves a mixture of charcoal and ash.

3. Aqueous rubian evaporated by heat in contact with the *air*, deposits dark brown resinous drops, the quantity of which increases on pouring water upon the residue, and again evaporating. The drops of resin melt in boiling water, become brittle on cooling, yield when heated in a test-tube, a copious yellow, transparent sublimate, resembling rubiacin, and behaving in a similar manner to ferric chloride; they are probably, therefore, a mixture of rubiretin and rubiacin.

4. *Oil of vitriol* dissolves rubian, with blood-red colour, and blackens it on boiling, with evolution of sulphurous acid.

5. When aqueous rubian is boiled with dilute *sulphuric* or *hydrochloric acid*, the solution first becomes opalescent, and then deposits orange-coloured flocks, containing alizarin, rubiretin, verantin, and rubianin, while sugar remains in solution.

a. Formation of alizarin :

$$C^{56}H^{34}O^{30} = 4C^{14}H^5O^4 + 14HO. \text{ (Schunck)}.$$
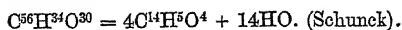
b. Formation of verantin and rubiretin :

$$C^{56}H^{34}O^{30} = 2C^{14}H^5O^5 + 2C^{14}H^6O^4 + 12HO. \text{ (Schunck)}.$$
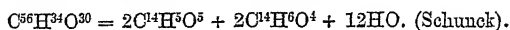
c. Formation of rubianin and sugar :

$$C^{56}H^{34}O^{30} + 9HO = C^{32}H^{19}O^{15} + 2C^{12}H^{12}O^{12} \text{ (Schunck)}.$$
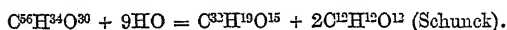
6. When *chlorine gas* is passed into aqueous rubian, the liquid, which is at first yellow, deposits lemon- and orange-yellow flocks of chlororubian, mixed with a small quantity of easily fusible resin, till it becomes colourless, and then contains sugar, together with excess of chlorine :

$$C^{56}H^{34}O^{30} + 6HO + 2Cl = C^{44}ClH^{37}O^{24},HCl + C^{12}H^{12}O^{12}.$$
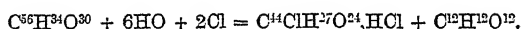
The continued action of the chlorine at length produces perchloro-rubian.—*Chloride of lime* converts rubian into phthalate of lime.

7. Aqueous rubian is not altered by cold *nitric acid*, but at the boiling heat, red fumes are evolved, and the rubian is completely converted into phthalic acid (xiii, 10) without formation of oxalic acid, or of any insoluble residue.

8. In contact with the aqueous solutions of *alkalis, alkaline earths,* or the *bicarbonates of alkaline earths,* and *air,* rubian takes up oxygen, and is converted into rubianic acid, rubidehydran, and rubihydran, small quantities of acetic acid, rubiadin, and sugar being formed at the same time.

a. Formation of rubianic acid :

$$\alpha. \quad C^{56}H^{34}O^{30} + 10O = C^{52}H^{29}O^{27} + 4CO^2 + 5HO.$$

$$\text{or } \beta. \quad C^{56}H^{34}O^{30} + 2O = C^{52}H^{29}O^{27} + C^4H^4O^4 + HO.$$

b. Of rubidehydran :

$$C^{56}H^{34}O^{30} = C^{56}H^{32}O^{28} + 2HO.$$

c. Of rubihydran :

$$C^{56}H^{34}O^{30} + 5HO = C^{56}H^{39}O^{35}.$$
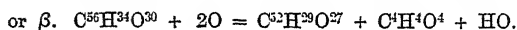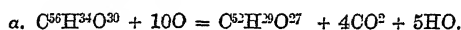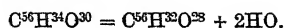
4·1049 grammes of rubian, in contact with hydrate of baryta and oxygen, absorbed 147 cc. oxygen in 143 days (= 5·16 p.c. O.), and formed therewith rubianic acid and rubidehydran, together with small quantities of alizarin, sugar and acetic acid. The equation *a, a* requires 13·1, β 2·62 p.c. oxygen absorbed.

9. Rubian boiled with excess of *caustic potash* or *soda,* dissolves with blood-red colour, changing to purple-red, and by continued boiling is completely resolved into alizarin, rubiretin, verantin, and rubiadin, which are precipitable by acids, and sugar which remains in solution. The same products are formed, though more slowly, by boiling with *caustic baryta.*—Formation of alizarin, rubiretin and verantin (vid. sup.) ; that of rubiadin is represented by the equation,

$$C^{56}H^{34}O^{30} + 2HO = 2C^{12}H^{12}O^{12} + C^{32}H^{10}O^8.$$
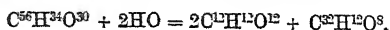
10. Rubian in alkaline solution reduces *gold-salts.*

11. *Erythrozym*, added to an aqueous solution of rubian, diffuses itself through the liquid without dissolving, rendering it turbid and gummy, and converting it, after standing for some time in a moderately warm place, into a brown jelly, like coagulated blood, containing yellow striæ and flocks formed of long capillary crystals, till finally (more erythrozym being added if necessary) the liquid becomes tasteless and colourless, and a gelatinous mass separates, consisting of alizarin, verantin, rubiretin, rubiafin, rubiagin, and rubiadipin. The solution retains sugar and pectic acid. During the fermentation, the liquid remains neutral, neither absorbing nor giving off gases : access of air is likewise unnecessary. — Formation of alizarin, verantin, rubiretin (p. 36); of rubiafin :

$$C^{56}H^{34}O^{30} + 3HO = C^{32}H^{13}O^{9} + 2C^{12}H^{12}O^{12}.$$

Formation of rubiagin :

$$C^{56}H^{34}O^{30} + 4HO = C^{32}H^{14}O^{10} + 2C^{12}H^{12}O^{12}.$$
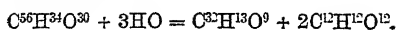
When a solution of rubian is boiled with erythrozym, no decomposition takes place. Erythrozym, after being dried and heated over the water-bath, decomposes rubian after two months only, into sugar, rubiafin, rubiretin, and verantin, without formation of alizarin. When dried at mean temperature, it decomposes rubian in a few days, forming sugar, rubiafin, rubiagin, and alizarin, together with small quantities of rubiretin and verantin. — The action of erythrozym on rubian is somewhat altered : a. *By a very small quantity of sulphuric acid.* Partial decomposition slowly sets in, yielding large quantities of rubiretin and verantin, with traces of alizarin and rubiagin. — b. *By carbonate of soda.* It dissolves in the red liquid. The decomposition which soon follows, yields more alizarin and rubiafin, no rubiagin, moderate quantities of rubiretin and verantin. — c. *By caustic soda.* A moderate quantity of caustic soda retards the action by which the rubiretin and verantin are chiefly produced. — d. *By neutral acetate of lead.* The erythrozym is precipitated in brown flocks, but decomposition gradually sets in, resulting in the formation of rubiafin, with traces of alizarin, and very large quantities of rubiretin and verantin. — e. *By mercuric chloride* or *arsenious acid.* A portion of the rubian remains undecomposed, even after several days : the products of the reaction which takes place are chiefly verantin and rubiretin. — f. *By alcohol* or *oil of turpentine.* They retard the decomposition, but increase the amount of rubiretin and verantin produced. — It appears then that retardation of the action of the erythrozym tends to produce less alizarin, and more rubiretin and verantin. When equal quantities of rubian mixed with carbonate of soda and with dilute sulphuric acid, were treated with erythrozym, a larger proportion of the rubian remained undecomposed in the first case than in the second ; nevertheless, in the first case, the quantity of alizarin formed amounted to 17·7 p. c. of the rubian employed, while, in the second, it was only 9·5 p. c.

A solution of rubian is not decomposed by yeast, gelatin, or putrefying albumin. It is decomposed by emulsin, whereby, in one instance, large quantities of alizarin, rubiretin and verantin were obtained. It is partially decomposed by the albuminous matter of *Helianthus tuberosus*, with formation of rubiretin and verantin.

Combinations. Rubian is very soluble in *water.* The solution is not precipitated by *acids;* neither is it altered by boiling with *phosphoric, oxalic, acetic,* or *tartaric acid;* nor precipitated by *acetate of alumina, alum, acetate of zinc, neutral acetate of lead, neutral* or *basic acetate of copper, bichloride of tin, mercurous nitrate, mercuric chloride, nitrate of silver, terchloride of gold,* nor coloured darker by any of these salts. Impure rubian is precipitated by acids and salts in brown resinous drops and flocks, which, when thrown down by acids, are soluble in pure water. An aqueous solution of rubian is coloured blood-red by *ammonia,* the liquid not being altered in colour by boiling, nor precipitated by acids; blood-red by *caustic soda,* changing to yellow after neutralisation with acids. With *baryta-* and *lime-water* it forms dark red precipitates soluble in pure water; it is coloured dark red by *magnesia,* and dissolves a portion of that base. It is completely or in great part precipitated by the *hydrates of alumina, ferric oxide,* and *cupric oxide.*

Lead-compound. An alcoholic solution of rubian is precipitated by neutral acetate of lead and a small quantity of ammonia, in such proportion that some of the rubian may still remain dissolved, and the light-red precipitate (which may also be obtained with basic acetate of lead) is washed with alcohol.

				Schunck.			mean; at 100°.
Calculation according to Schunck.							
56 C	....	336	....	26·25	....	26·02
34 H	....	34	....	2·65	....	2·74
30 O	....	240	....	18·76	....	18·61
6 PbO	....	670	..... .	52·34	....	52·63

$C^{56}H^{34}O^{30},6PbO$ .... 1280 .... 100·00 .... 100·00

Schunck overlooks the fact that the lime attached to the rubian may pass into this compound (*Ann. Pharm.* 81, 344).

Rubian is somewhat less soluble in *alcohol* than in water. *Ether* does not dissolve it, but, on the contrary, precipitates it from the alcoholic solution.

From the aqueous solution, rubian is precipitated by *porous* and *finely divided bodies.* This action is exerted especially by *protosulphide of tin;* less strongly by the *sulphides of lead* and *copper,* the action of these bodies being most powerful when they are formed in the solution itself; by *soot,* and, above all others, by *animal charcoal.* The rubian may be separated by boiling with alcohol, not completely, however, from animal charcoal, excepting when only a small quantity of charcoal has been used to a large quantity of rubian. Rubian imparts a light orange colour to stuffs prepared with alum mordants; light brown to those mordanted with iron; stuffs prepared with other mordants are but faintly dyed by it.

Rubianic Acid.

$$C^{52}H^{29}O^{27}.$$
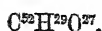
Ed. Schunck (1856). *N. Phil. Mag. J.* 12, 200 and 270; *J. pr. Chem.* 70, 154. — Preliminary Notice: *Chem. Gaz.* 1855, 357; *J. pr. Chem.* 67, 154.

Formation (p. 36). Rubian, in contact with air and aqueous ammonia, caustic soda, baryta, lime, or bicarbonate of baryta, is resolved, with assumption of oxygen, into a rubianate, rubidehydran, and rubihydran. A similar, but less powerful action, is exerted by oxide of lead.

Preparation. 1. *From Rubian.* Carbonic acid gas is passed into a solution of rubian mixed with excess of baryta-water, till the baryta is converted into bicarbonate, and the filtrate is left to stand in contact with the air. The liquid, after some time, becomes covered with thin scarlet films, presenting a crystalline appearance under the microscope (compounds of baryta with rubianic acid and rubidehydran), more of which are obtained after longer standing, and again on evaporating the liquid, finally in the form of red flocks, whilst rubihydran remains dissolved in the brownish-yellow liquid (sometimes also sugar resulting from a secondary decomposition). The collected films and flocks are decomposed with dilute sulphuric acid; the excess of that acid is precipitated by carbonate of lead; the precipitate is repeatedly boiled with water, till it exhibits only a faint reddish tint (in which state it contains no impurity except a small quartity of rubiadin, produced by secondary decomposition), and the solution is filtered and evaporated; a yellow-brown mass then remains, mixed with yellow needles, from which cold water extracts rubidehydran, leaving rubianic acid in the form of a yellow powder. This product is washed with cold water, and recrystallised from boiling water, if necessary, with aid of animal charcoal.

2. *From Madder, without previous preparation of rubian.* — Extract of madder prepared with hot water is precipitated with neutral acetate of lead, then the filtrate with basic acetate; and the latter precipitate containing rubian and chlorogenin, is decomposed with cold dilute sulphuric acid, digested with carbonate of lead, and filtered. The filtrate, treated with baryta-water, then with carbonic acid, as in the first method, deposits, after standing for some time in contact with the air, rubianate of baryta, and the baryta-compound of rubidehydran, to be treated as in 1, while rubidehydran and chlorogenin remain in solution.

Properties. Lemon-yellow silky needles; in the impure state, granules and crystalline mass. Tastes somewhat bitter. Reddens litmus.

							Schunck.
Calculation according to Schunck.							
52	C	312	....	56·01	....	55·52	to	56·58
29	H	29	....	5·20	....	5·36	....	5·61
27	O	216	....	38·79	....	39·12	....	37·81
$C^{52}H^{29}O^{27}$		557	....	100·00	....	100·00	....	100·00

Schunck analysed rubianic acid prepared with ammonia, caustic soda, lime and carbonate of baryta. — It is perhaps identical with Rochleder's ruberythric acid (p. 42).

Decompositions. 1. Melts when *heated* in a tube, or between two watch-glasses, to a brown-red liquid, which solidifies in the crystalline form; at a stronger heat, it gives off vapours, which condense to orange-coloured needles of alizarin, and leaves charcoal. — 2. Heated on platinum-foil, it melts and *burns* away incompletely, with a smoky

flame. — 3. By boiling with dilute *sulphuric* or *hydrochloric acid*, it is resolved into alizarin and sugar, the former separating in dark yellow flocks. 100 pts. rubianic acid yield 42·47 pts. of alizarin, therefore $C^{52}H^{29}O^{27} + 5HO = 2C^{14}H^{5}O^{4} + C^{24}H^{24}O^{24}$ (Schunck), calc. = 43·44 p. c. Cold oil of vitriol dissolves rubianic acid with dark red colour; boiling oil of vitriol dissolves it with dark red-brown colour, and evolution of a small quantity of sulphurous acid. — 4. Aqueous rubianic acid is decolorised by *chlorine*, then exhibits a milky turbidity, and separates brownish-yellow crystals. — Solution of *chloride of lime* first colours it blood-red, then decolorises it. — 5. With cold *nitric acid*, it forms a yellow solution, which, on boiling, gives off nitrous gas, and becomes colourless, and on evaporating leaves oxalic acid and a brown syrup.— 6. By boiling with excess of caustic *alkalis*, it first becomes purple, afterwards violet and opaque, and then yields with acids a flocculent precipitate of alizarin (mixed with undecomposed rubianic acid, if the boiling has not been continued long enough), while sugar remains in solution; 100 pts. rubianic acid yield 45·17 pts. alizarin (calc. 43·44 pts., according to the equation given under 3). — 7. Rubianic acid boiled with an aqueous solution of *ferric chloride*, dissolves, with greenish brown colour, producing a small quantity of ferrous chloride, and when the solution is evaporated, yields a small quantity of black powder, probably consisting of a compound of alizarin with ferric oxide. — 8. When boiled with aqueous *terchloride of gold* and a few drops of ammonia, it is decomposed, with separation of gold.—9. When *erythrozym* is added to water in which rubianic acid is suspended, the acid is gradually resolved into alizarin and sugar.

Combinations. Rubianic acid dissolves more easily in boiling than in cold *water*, and separates in the crystalline state. It dissolves without decomposition in hot aqueous *phosphoric, acetic, oxalic,* and *tartaric acids*.

With salifiable bases it forms the *Rubianates*.

Rubianate of Ammonia.—Rubianic acid forms with ammonia, less easily than with aqueous fixed alkalis, a red solution, which is not altered by boiling, and when evaporated leaves the ammonia-salt in the form of a red gum, mixed with a little free rubianic acid.—By adding carbonate of ammonia to boiling aqueous rubianic acid, and cooling the solution, it is obtained in needles, like the potash-salt. — It does not give off ammonia in drying. In hot water it is decomposed like the potash salt.

Rubianate of Potash.—Concentrated aqueous rubianic acid mixed with caustic potash ley, acquires a cherry-red colour, and remains clear; carbonate of potash precipitates from it dark red needles of rubianate of potash, which, after washing and drying, exhibit a silky lustre and flea-brown colour, and over the water-bath or in vacuo, assume a transient light red colour. It is decomposed by cold, more easily by boiling water, with separation of free rubianic acid.

Calculation according to Schunck.				Schunck. *at* 100° ; *mean.*	
52 C	 312	....	52·42	....	52 02
28 H	 28	....	4·70	.... ..	4·84
26 O	 208	....	34·97	....	35·56
KO	.... 47·2	....	7·91	....	7·58
$C^{52}KH^{28}O^{27}$............ 595·2		....	100·00	....	100·00

Rubianate of Soda.—Hot aqueous rubianic acid, mixed with caustic soda or carbonate of soda, yields on cooling light red granules of the soda-salt, which dissolve sparingly in cold water, with red colour in hot water, and separate on cooling in the form of a thick jelly, on which crystals of rubianic acid gradually form.

Rubianate of Baryta. — a. *Mono-acid.* — 1. Baryta-water forms a crimson-red precipitate with aqueous rubianic acid, and decolorises it. The precipitate dissolves on passing carbonic acid into the liquid, forming a yellow solution, which, on standing in contact with the air, deposits the salt in films, exhibiting a crystalline character under the microscope. — 2. Rubianate of potash is precipitated by chloride of barium, and the red precipitate is washed and dried in vacuo.

According to 2.				Schunck. *mean.*
52 C	 312	....	49·24	.... 48·63
29 H	 29	....	4·57	.... 4·75
27 O	 216	....	34·11	.... 34·93
BaO	... . 76·5	....	12·08	.... 11·69
$C^{52}BaH^{28}O^{27}$ + Aq. .... 633·5		....	100·00	.... 100·00

b. *Sesqui-acid?* — The red precipitate which an ammoniacal solution of rubianic acid forms with chloride of barium, loses baryta in washing, and then contains 3 at. acid to 2 at. baryta.

Rubianate of Lime. — Lime-water added to aqueous rubianic acid forms a light red precipitate soluble in carbonic acid, and not reappearing in the solid state when the carbonic acid escapes, but only when the solution is evaporated.

Rubianate of Lead.—Alcoholic, but not aqueous, rubianic acid throws down from a solution of neutral acetate of lead, red flocks soluble in pure water. — Alcoholic rubianic acid mixed with ammonia and an insufficient quantity of neutral acetate of lead, yields red flocks, which after washing with alcohol, drying in vacuo, and then over the water-bath, contain $7PbO,2C^{52}H^{27}O^{25}$. — From basic acetate of lead, alcoholic rubianic acid throws down a precipitate = $9PbO,C^{52}H^{27}O^{26}$, which, after solution in alcoholic acetic acid and precipitation with ammonia, contains 6 at. lead oxide to 1 at. ammonia.

Aqueous rubianic acid is precipitated by *hydrate*, but not by *acetate of alumina*, by *ferric hydrate*, but not by *ferric chloride*. — *Cupric acetate* forms, both in aqueous and in alcoholic rubianic acid, a brownish red precipitate, soluble in boiling acetic acid.

Rubianate of Silver. — Nitrate of silver does not alter boiling rubianic acid, but on addition of ammonia it throws down red-brown flocks, which appear crystalline under the microscope, and form with ammonia a red solution, which does not alter, even at the boiling heat. The

salt, after washing with a small quantity of water, then with alcohol, and drying in vacuo, contains 17·58 p. c. AgO. ($C^{52}H^{28}O^{26}$, AgO = 17·47 p. c.)

Rubianic acid dissolves in *alcohol*, but not in *ether*. It does not dye mordanted fabrics.

Ruberythric Acid.

$C^{72}H^{40}O^{40}$ or $C^{56}H^{31}O^{31}$?
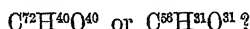
ROCHLEDER.   See the memoirs cited under Alizarin, xiv, 130.

Occurrence. In madder-root.— Schunck found no ruberythric acid in madder, and is of opinion that in the preparation of ruberythric acid, products of the decomposition of rubian must have been obtained.

Preparation. The aqueous decoction of madder-root is precipitated by neutral acetate of lead; the precipitate (which serves for the preparation of alizarin and purpurin, xiii, 327), is collected on a filter; and the filtrate is mixed with basic acetate of lead, not in excess, which throws down a dark flesh-coloured, nearly brick-red precipitate, containing ruberythric and rubichloric acids, with small quantities of citric and phosphoric acids. This precipitate is suspended in water, and decomposed by hydrosulphuric acid, the solution chiefly containing rubichloric acid is filtered from the sulphide of lead: and the ruberythric acid which remains attached to this lead-precipitate is extracted from it, after washing for a short time, by boiling with alcohol. The alcoholic solution evaporated to one-third, then mixed with water and a small quantity of baryta-water, deposits a scanty white precipitate, and the filtrate treated with a larger quantity of baryta-water yields ruberythrate of baryta in dark cherry-red flocks. These are collected and dissolved in dilute acetic acid; the solution is nearly neutralised with ammonia, and precipitated by basic acetate of lead, whereby a cinnabar-coloured lead-salt is obtained, which must be washed with dilute alcohol, and decomposed under alcohol by hydrosulphuric acid. The liquid heated to the boiling point with the sulphide of lead, then filtered hot and evaporated, deposits light yellow crystals of ruberythric acid, which may be purified by pressure, and recrystallisation from a small quantity of boiling water. 25lb. madder yield 1 gramme of the acid ; Levantine more than European madder.

Properties. Yellow prisms having a silky lustre, and not diminishing in weight by drying at 100°. Has a faint taste.

Calculation according to Rochleder.								Rochleder.
earlier.				*later.*				
72 C	432	....	54·54	56 C	336	....	54·64	.... 54·48
40 H	40	....	5·05	31 H	31	....	5·04	.... 5·16
40 O	320	....	40·41	31 O	248	....	40·32	.... 40·36
$C^{72}H^{40}O^{40}$	792	....	100·00	$C^{56}H^{31}O^{31}$	615	....	100·00	.... 100·00

Rochleder is undecided between these two formulæ : he regards Kuhlmann's xanthin, Higgin's xanthin, Schunck's xanthin (chlorogenin), and Runge's madder-

yellow, as impure ruberythric acid. It is more probably identical with Schunck's (more recently prepared) rubianic acid, though it is said to differ therefrom in composition and in the degree of its solubility in ether.

Decompositions. 1. The aqueous solution becomes turbid when heated with *hydrochloric acid,* and forms, on boiling, a yellow jelly, which cakes together into flocks of alizarin, while sugar remains in solution.

$$C^{72}H^{40}O^{40} = C^{12}H^{10}O^{10} + 3C^{20}H^6O^6 + 12HO.$$

$$\text{or, } C^{56}H^{31}O^{31} = 2C^{20}H^6O^6 + \tfrac{4}{3}C^{12}H^{12}O^{12} + 3HO \text{ (Rochleder).}$$
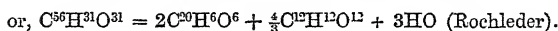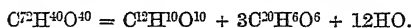
2. When the blood-red solution of ruberythric acid is boiled with *aqueous alkalis,* it acquires the colour of alkaline solutions of alizarin and deposits alizarin on addition of an acid. — 3. It is not altered by *emulsin.*

Combinations. Ruberythric acid dissolves sparingly in cold, easily in hot *water.*

In aqueous *alkalis* it dissolves with dark blood-red colour. The aqueous acid forms with *baryta-water* a dark cherry-red, flocculent precipitate ; with solution of *alum,* after addition of ammonia, a cinnabar-red precipitate.

Ruberythrate of Lead. — An aqueous solution of ruberythric acid mixed with a little alcohol, is precipitated by basic acetate of lead, the liquid is heated, and the precipitate washed with water containing alcohol. Cinnabar-red powder.

Calculation according to Rochleder.									Rochleder.	
	earlier.				*later.*				*in vacuo.*	
72 C	432	....	22·92	14 C		84	....	22·64	....	22·74
37 H	37	....	1·96	7 H		7	....	1·89	....	2·00
37 O	296	....	15·70	7 O		56	....	15·09	....	15·82
10 PbO	1120	....	59·42	2 PbO		224	....	60·38	....	59·44
$C^{72}H^{37}O^{27}$,10PbO..	1885	....	100·00	$C^{14}H^7O^7$,2PbO....		371	....	100·00	....	100·00

$$C^{14}H^7O^7,2PbO = \tfrac{1}{4}C^{56}H^{28}O^{28},\tfrac{1}{2}PbO \text{ (Rochleder).}$$
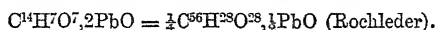
Ruberythric acid dissolves in boiling aqueous *ferric chloride,* forming a dark brown-red solution, which is precipitated by alcohol.

It dissolves with gold-yellow colour in *alcohol* and in *ether.*

Appendix to Rubian, Rubianic Acid, and Ruberythric Acid.

1. Rubihydran.

$$C^{56}H^{39}O^{35}?$$
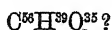
Ed. Schunck. *J. pr. Chem.* 70, 166.

When rubian is decomposed by bicarbonate of baryta for the preparation of rubianic acid and rubidehydran, this substance remains in solution after the baryta-compounds have been separated, and is purified as follows :—

1. The brown-yellow filtrate, obtained as described at page 39, 1, is again mixed with baryta-water to separate any still undecomposed rubian; carbonic acid is once more passed into it, and the red flocks which separate on evaporation are removed. The filtrate mixed with basic acetate of lead yields a red precipitate, which is to be washed, decomposed with cold dilute sulphuric acid, and treated with carbonate of lead to remove the excess of that acid. The precipitates are then removed; hydrosulphuric acid is passed into the liquid; the sulphide of lead is separated by filtration; and the filtrate is evaporated.

2. The solution of rubihydran and chlorogenin obtained as already described (p. 39, 2), is again precipitated with basic acetate of lead, and the precipitate is washed with water, dissolved in acetic acid, and reprecipitated by ammonia. The lead-precipitate thus produced is free from chlorogenin, and is decomposed for the preparation of rubihydran, like that obtained by method 1. If the rubihydran still retains chlorogenin, its solution turns green when boiled with hydrochloric or sulphuric acid.

Properties. Brown-yellow, transparent gum, having a bitter taste. It does not give off all its water till after prolonged heating over the water-bath, then becoming brittle and easy to pulverise; on exposure to the air it quickly becomes moist and soft.

					Schunck.
56 C	....	336	....	51 29	.... 51·5
39 H	...	39	....	5·95	.... 6·0
35 O	..	280	....	42 76	.... 42·5
$C^{56}H^{39}O^{35}$	....	655	....	100 00	.... 100 0

Rubihydran = Rubian + 5 aq.
In other experiments Schunck obtained numbers agreeing with the formulæ $C^{56}H^{39}O^{35}$ + 3 aq. and + 6 aq.

Decompositions. 1. Rubihydran *heated* in a glass tube yields a smaller quantity of crystalline sublimate than rubian. — 2. When boiled with dilute *sulphuric* or *hydrochloric acid*, it forms a turbid solution which deposits yellow flocks and drops of brown resin, and after boiling for some time, becomes colourless and is completely resolved into rubiretin, verantin, rubiadin, a small quantity of alizarin, and sugar. — 3. Boiled with aqueous *caustic potash* or *soda*, it forms a solution which is red at first, but soon deposits a few purple flocks and becomes yellowish-brown, and when treated with acids, loses its colour and deposits a yellow flocculent precipitate containing the same substances as those which are produced by boiling rubihydran with hydrochloric acid. This reaction does not yield rubianic acid like the corresponding reaction with rubian. — 4. With *chlorine* it yields the same products as rubian.

Combinations. Rubihydran dissolves readily in *water*. It is not altered by boiling *phosphoric, oxalic, acetic,* or *tartaric acid*. It is not precipitated by metallic salts, with the exception of basic acetate of lead.

Lead-compound. — Basic acetate of lead forms with aqueous rubi-

hydran a brownish-red precipitate, less fiery than those which it yields with rubian and rubidehydran; the supernatant liquid is light yellow, and is precipitated by ammonia in pale red flocks. — When alcoholic rubihydran is precipitated with ammonia and an insufficient quantity of neutral acetate of lead, the precipitate, after being washed with alcohol, dried in vacuo, and then over the water-bath, contains 20·98 p. c. C., 2·48 H., and 59·18 PbO ; therefore carbon and hydrogen in the proportions required by rubihydran $= C^{57}H^{39}O^{35}$, but the lead-oxide not in simple atomic proportion.

Rubihydran is not very soluble in *alcohol*.

2. Rubidehydran.

$$C^{56}H^{32}O^{28}.$$
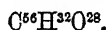
Ed. Schunck. *J. pr. Chem.* 70, 162.

The solution of rubidehydran obtained (p. 39) by decomposing rubian with bicarbonate of baryta (ammonia, lime, or baryta-water), is purified by evaporation, re-solution in cold water, and precipitation of the solution evaporated to a syrup, with alcohol, which separates a reddish-yellow, gummy mass, together with sulphates. The solution, filtered therefrom and evaporated, leaves rubidehydran, which however still retains the sulphates of lime, magnesia, and soda, from which Schunck does not attempt to purify it, for fear of decomposing it.

Properties. Reddish-yellow, transparent gum. Not deliquescent. Has a strong bitter taste.

Calculation according to Schunck.				Schunck. mean.
56 C	336	....	56·75	.... 56·50
32 H	32	....	5·40	.... 5·65
28 O	224	....	37·85	.... 37·85
$C^{56}H^{32}O^{28}$	592	....	100 00	.... 100·00

Rubidehydran = Rubian − 2aq., after deduction of ash. Similar results were obtained with rubidehydran prepared with bicarbonate of baryta, or with ammonia, lime, or caustic baryta.

Decompositions. Rubidehydran boiled with dilute *sulphuric* or *hydrochloric acid*, is resolved into a mixture of sugar, alizarin, rubiadin, a small quantity of verantin and rubiretin, without production of rubianin. — When boiled with *alkalis*, it forms a purple-red solution, from which acids throw down yellow flocks. No rubianic acid is formed in this reaction (except when caustic baryta is used). — With aqueous *chlorine* it yields the same products as rubian.

Combinations. Rubidehydran dissolves in water, forming a yellow solution which is not precipitated by any metallic salt, except basic acetate of lead.

Lead-compound. — Alcoholic rubidehydran forms a yellow precipitate

with alcoholic neutral acetate of lead. To prepare the salt, a very strong aqueous solution of rubidehydran is mixed with alcoholic sugar of lead, the red precipitate is separated by filtration; the filtrate is precipitated by ammonia; and the precipitate is washed with alcohol.

After drying over the water-bath, it contains 29·2 p. c. C., 2·85 H., 47·73 PbO. and 14·7 MgO.; which latter Schunck regards as taking the place of a certain portion of lead-oxide : hence he gives the formula $5PbO,C^{56}H^{32}O^{28}$.

Chlororubian.

$$C^{44}ClH^{27}O^{24}.$$
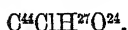
ED. SCHUNCK (1855).   *N. Phil. Mag. J.* 12, 200 and 270; *J. pr. Chem.* 70, 169.   Preliminary Notice : *Chem. Gaz.* 1850, 357 ; *J. pr. Chem.* 67, 154; *Pharm. Centr.* 1855, 785.

Formation. By the action of chlorine in aqueous rubian (p. 36).

Preparation. An aqueous extract of madder is precipitated by neutral acetate of lead, the filtrate precipitated with ammonia; the resulting red precipitate decomposed by sulphuric acid ; and chlorine gas passed into the filtrate. The dirty yellow flocks of an easily fusible resin, which are precipitated by the first action of the chlorine, are separated by filtration; and the pure yellow flocks of chloro-rubian, precipitated on continuing the passage of the chlorine, are collected and crystallised from hot alcohol.

Properties. Crystallised from a dilute alcoholic solution, it forms light orange-yellow needles, having a bitter taste ; precipitated from a concentrated alcoholic or hot aqueous solution, it forms granulo-amorphous spherules.   Neutral.

	Calculation according to Schunck.				Schunck. mean ; at 100°.
44 C	264·0	....	50·92	....	51·18
Cl	35·5	....	6·82	....	6·38
27 H	27·0	....	5·20	....	4·93
24 O	192·0	....	37·06	....	37·51
$C^{44}ClH^{27}O^{24}$	518·5	....	100·00	....	100·00

Decompositions. 1. *Heated* in a test-tube, it melts to a brown liquid, yields a white crystalline sublimate, and leaves charcoal. — 2. On platinum-foil, it melts and *burns* with a smoky, greenish flame, leaving a large quantity of charcoal. — 3. *Chlorine-water* gradually converts it into perchlororubian. — 4. With boiling dilute *sulphuric* or *hydrochloric acid*, it forms at first a yellow solution, which, on continued boiling, becomes milky, and deposits yellow flocks of chloro-rubiadin, while sugar remains in solution :

$$C^{44}ClH^{27}O^{24} = C^{32}ClH^{12}O^9 + C^{12}H^{12}O^{12} + 3HO.$$
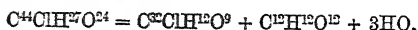
5. With aqueous *caustic soda*, it forms a blood-red solution, which,

after being heated for some time, deposits dark red-brown flocks of oxyrubian (*q. v.*), while sugar, its products of decomposition, and verantin, rubiretin and rubiadin remain dissolved.

The red liquid which remains after the separation of the oxyrubian, yields, with dilute sulphuric acid, a yellowish brown precipitate and a filtrate, which (after saturation with carbonate of lead, and separation of the sulphate of lead) leaves, on evaporation, sulphate of soda, chloride of sodium, and a brown saccharine syrup. — The yellowish brown precipitate produced by dilute sulphuric acid, dissolves in alcohol, with the exception of a portion, *a*; the solution forms with neutral acetate of lead, a brown precipitate, *b*; and the liquid filtered therefrom, yields, with water, yellow-flocks, *c.* — *a* is dark-brown, black when dry, and contains 67·56 p. c. C., 4·1 H., and 28·35 O.; probably, therefore, a product of the decomposition of sugar and of Mulder's ulmic acid. — *b*, boiled with hydrochloric acid, after washing with alcohol, deposits brown flocks, which yield to cold alcohol, rubiretin or some substance of that nature, while verantin remains dissolved; these flocks, after solution in alcoholic ammonia, and precipitation with acetic acid, contain 64·8 p. c. C. and 4·3 H. — *c* yields to alcohol impure rubiadin (containing 68·86 p. c. C. and 5·4 H.), and leaves brown flocks. — 6. Chlororubian, dissolved in potash-ley reduces *auric chloride* in the cold.

Chlororubian dissolves with yellow colour in boiling *water*.

With *alkaline carbonates*, it forms a clear blood-red solution (*vid. sup.*); with *baryta-water*, on boiling, dark red flocks; with *chloride of calcium* and ammonia, a light red precipitate, the supernatant liquid being nearly colourless in both cases. — Aqueous chlororubian does not precipitate *acetate of alumina* or *ferric hydrochlorate*; but solid chlororubian dissolves in boiling ferric chloride with bluish yellow and then with darker colour, and ultimately deposits a black powder. — Its alcoholic solution does not precipitate alcoholic *neutral acetate of lead* or *acetate of copper;* but aqueous chlororubian forms, with *basic acetate of lead,* a light red precipitate and a red liquid.

Chlororubian is soluble in *alcohol.* It does not dye mordanted tissues.

Appendix to the Glucosides of Madder.

Compounds either produced by the decomposition of these Glucosides, or existing ready-formed in the Madder.

1. Rubiacin.

$$C^{32}H^{11}O^{10}.$$
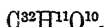
Runge. *J. pr. Chem.* 5, 367.
Robiquet. *Ann. Chim. Phys.* 63, 311.
Higgin. *Phil. Mag. J.* 33, 232 ; *J. pr. Chem.* 46, 1.
Ed. Schunck. See Memoirs cited under Rubian, 1 and 3.

Madder-orange. Krapp-orange. — Observed by Runge and Robiquet, investigated by Schunck. It is not yet decided whether Higgin's rubiacin is identical with the body which Schunck designates by this name.

Occurrence. In madder-root; perhaps as a soluble lime-compound from which the rubiacin separates as the madder-extract turns sour (Schunck).

Formation. 1. By the action of alkaline hydrosulphates on rubiacic acid (Schunck). — 2. Higgin's xanthin is converted, when the aqueous extract of madder is left to stand, first into rubiacin, then into alizarin (Higgin). — 3. By heating a solution of xanthin in oil of vitriol till it assumes a carmine-red colour (Higgin).

Preparation. a. *From Madder.* 1. By Higgin's method (xiv, 136).

2. It is found partly in the precipitate produced by acids in the decoction of madder (p. 34, *Preparation of Rubian*), partly in the residue left after exhausting the root with water, and may be obtained in the pure state by conversion into rubiacic acid, and subsequent reduction from this compound (pp. 34 and 50) (Schunck).

3. Madder-root freed from parenchyma (*le meditullium ligneux*) is exhausted with cold ether, and three-fourths of the ether is distilled off from the extract; rubiacin then separates at the bottom of the retort, as an orange-yellow crystalline deposit (Robiquet).

4. Madder-root rinsed, but not comminuted, is macerated at 15° with 8 pts. of water for sixteen hours, and the residue then treated with an equal quantity of water. The united extracts then deposit, after four to six hours, small crystals of madder-orange, which are collected, washed with cold water, and recrystallised from boiling alcohol. till a sample dissolves in oil of vitriol with pure yellow colour (Runge). Schunck obtained rubiacin by treating pulverised madder on a cloth with a small quantity of cold water, collecting the crystals which separated, after 12 hours' standing, from the then acid liquid (after longer standing, verantin also separates), and purifying them by treatment with dilute nitric acid (which does not attack rubiacin), and recrystallisation from alcohol.

b. *From Rubiacic acid.* The boiling aqueous solution of rubiacate of potash is mixed with a slight excess of caustic potash; hydro-sulphuric acid passed into the solution for a considerable time, and the liquid precipitated with chloride of barium. The purple precipitate of rubiacin-baryta, when washed with cold water and decomposed by hydrochloric acid, leaves rubiacin, which may be purified by solution in boiling alcohol and recrystallisation (Schunck).

c. *From the Madder-liquor of the dye-houses.* The liquid is mixed with hydrochloric acid; the precipitate treated with boiling alcohol; the orange-yellow powder which separates on cooling, from the result-ing deep yellow solution is re-dissolved in boiling alcohol; hydrated protoxide of tin is added; and the liquid is filtered hot; rubiacin then separates on cooling in light yellow needles.

Properties. Splendid plates and needles, with strong, reddish-green lustre, like iodide of lead (Schunck). Yellow crystalline powder (Runge). Yellow, paper-like laminæ, made up of fine needles (Robiquet). When carefully

heated, it volatilises completely, and sublimes in yellow scales (Schunck). Leaves charcoal when sublimed (Runge, Robiquet, Higgin).

				Schunck.		
				a.		*b. mean.*
32 C	192	....	67·84	.... 67·01	......	67·1
11 H	11	....	3·88	.... 3·28	....	4·0
10 O	80	....	28·28	...... 29·71	......	28·9
$C^{32}H^{11}O^{10}$	283	....	100·00	.... 100·00	....	100·0

Schunck formerly gave the formula $C^{31}H^9O^{10}$ calculated from analysis *a*.

Decompositions. 1. Melts when *heated* on platinum-foil, and burns with a smoky flame, leaving no residue (Schunck). — 2. Heated with *oil of vitriol,* it forms a dark brown solution, and is precipitated by water as a brown powder destitute of colouring properties (Higgin); see below. — 3. Dissolves without alteration in boiling dilute *nitric acid,* and is decomposed with difficulty by boiling with the concentrated acid. — 4. A boiling aqueous solution of *ferric nitrate* or *hydrochlorate* dissolves it without alteration at first, but converts it into rubiacic acid, after continued boiling. — 5. By *alkaline hydrosulphates.* it appears to be converted into rubiafin. According to Schunck's earlier experiments, rubiacic acid treated with hydrosulphuric acid is converted into rubiacin; but according to later experiments, the product thus obtained is a substance resembling rubiacin or rubiafin, and containing 70·24 p. c. C., 4·64 H., and 25·12 O., therefore $C^{32}H^{12·5}O^{8·5}$, that is to say, rubiafin — ½ at. aq.; hence Schunck supposes that the rubiacic acid is first converted into rubiacin, and then this latter into rubiafin.

Combinations. Rubiacin dissolves sparingly in boiling *water,* forming a reddish yellow liquid (amber-yellow, according to Higgin), whence it crystallises on cooling (Schunck and others).

It is slightly soluble in dilute *acids* (Higgin).

It dissolves in *oil of vitriol,* without decomposition, even at the boiling heat, forming a yellow solution, whence it is precipitated by water (Schunck). Vide sup. The solution in cold oil of vitriol is yellow (Runge), reddish-yellow (Robiquet), orange-yellow (Higgin).

Rubiacin dissolves with brownish colour in *ammonia* (Robiquet). It dissolves also in a warm ammoniacal solution of *sulphate of ammonia* (Higgin).

In *caustic alkalis* it dissolves with rose-red colour (Runge, Robiquet), with fine crimson archil-colour (Higgin), with purple colour, and is precipitated by acids (Schunck).

With *carbonate of soda* it forms an orange-coloured solution (Runge), which becomes blood-red on boiling, and deposits red flocks as it cools (Schunck).

With *lime* it forms a very soluble compound (Higgin, Schunck). The solution of rubiacin in ammonia forms dingy red precipitates with the chlorides of barium and calcium (Schunck).

When boiled with *solution of alum,* it forms a light orange-coloured solution (Runge), without any tinge of red, and is precipitated in greenish yellow flocks by sulphuric acid. The alum-solution does not become turbid on cooling, unless a large quantity of alizarin is present at the same time, in which case the greater part of the rubiacin is likewise precipitated (Higgin). *Hydrate of alumina* immersed in an

alcoholic solution of rubiacin, acquires an orange colour, and precipitates it completely. The precipitate dissolves easily, and with purple colour in caustic potash (Schunck).

Lead-compound. An alcoholic solution of rubiacin forms a dark red precipitate with an alcoholic solution of neutral acetate of lead (Schunck).

						Schunck.
96 C	....	576	....	33·05	....	33·05
33 H	....	33	....	1·89	....	1·80
30 O	....	240	....	13·78	....	14·41
8 PbO	....	896	....	51·28	....	50·74
$3C^{32}H^{11}O^{10},8PbO$....		1745	....	100·00	....	100·00

Rubiacin dissolves sparingly in cold, more abundantly in boiling *alcohol*, and is precipitated in yellow flocks by water (Schunck). Nearly insoluble in cold alcohol, but dissolves sparingly in boiling alcohol, forming a golden-yellow solution (Robiquet). Easily soluble in alcohol (Higgin).

Dissolves easily in *ether* (Robiquet, Higgin), sparingly in *acetic acid* (Robiquet). It colours mordanted tissues slightly (Schunck), not at all (Higgin), brilliant orange-yellow (Runge).

2. Rubiafin.

$$C^{32}H^{13}O^9.$$

SCHUNCK. *J. pr. Chem.* 59, 465.

Formation. In the fermentation of rubian (p. 37).

Preparation. (xiv, 135.)

Yellow shining plates and needles, sometimes star- or fan-shaped masses, which behave like rubiacin when heated with water, sulphuric acid, nitric acid, neutral acetate of lead, and cupric acetate, and likewise form rubiacic acid when treated with ferric nitrate: hence rubiafin differs from rubiacin only in composition.

						Schunck.
32 C	....	192	....	69·31	....	69·30
13 H	....	13	....	4·69	.. ..	4·56
9 O	....	72	....	26·00	... .	26·14
$C^{32}H^{13}O^9$.	....	277	....	100·00	... ...	100·00

3. Rubiacic Acid.

$$C^{32}H^9O^{17}.$$

ED. SCHUNCK (1848). *Ann. Pharm.* 66, 201; abstr. *Pharm. Centr.* 1848, 609 and 625; *Compt. Chim.* 1849, 215.—*N. Phil. Mag.* 5, 410 and 495; *J. pr. Chem.* 59, 453: abstr. *Ann. Pharm.* 87, 344.

Formation. By boiling rubiafin or rubiacin with an aqueous solution of ferric nitrate or chloride.

Preparation. From Madder (p. 34). —*From the liquor which has been used for dyeing with madder, and still contains madder. Spent madder-liquor.* This brown, muddy liquid, after the woody particles of the madder have been removed from it, is mixed with hydrochloric acid; the brown flocks which fall down are boiled with ferric nitrate as long as anything is thereby dissolved; and the dark red-brown filtrate is precipitated by an acid: a yellow precipitate is then obtained, consisting of a mixture [or a compound (p. 52)] of rubiacin and rubiacic acid. This mixture, or the red rubiacin obtained as already described (p. 34), is boiled for a long time with aqueous ferric nitrate; the solution is precipitated with hydrochloric acid; and the precipitate is first washed with water and then with boiling alcohol, which dissolves the unaltered rubiacin, and leaves behind the rubiacic acid that has been formed. By evaporating the alcoholic solution and repeatedly boiling the residue with ferric nitrate, the whole of the rubiacin may be ultimately converted into rubiacic acid. The rubiacic acid obtained by this process, or in the preparation of rubian (xiv, 134), is converted into potash-salt by solution in boiling aqueous carbonate of potash, filtration, and evaporation, and the potash-salt is purified by recrystallisation, and decomposed by hydrochloric acid. If the rubiacic thus obtained is still contaminated with rubiacin, it will yield by careful sublimation between two watch-glasses, a yellow sublimate, of which the pure acid yields no more than a mere trace.

Properties. Non-crystalline, lemon-yellow powder.

					Schunck.		
					earlier; mean.		later; mean.
32 C	192	....	56·97	....	57·28	....	57·59
9 H	9	....	2·67	....	2·47	....	2·87
17 O	136	....	40·36	......	40·25	.....	39·54
$C^{32}H^9O^{17}$	337	....	100·00	....	100·00	....	100·00

Decompositions. 1. *Heated* on platinum foil, it melts and *burns* with a bright flame, leaving no residue. — 2. *Heated* in a test-tube, it gives off vapours and oil, but no crystalline sublimate. Between watch-glasses, a trace of sublimate is obtained, and a large quantity of charcoal. (Vid sup.) — 3. It dissolves in cold *oil of vitriol*, forming a yellow solution precipitable by water: in hot oil of vitriol, with decomposition, the solution no longer yielding a precipitate with water. — 4. With strong *nitric acid* it forms a yellow solution, which is decomposed on heating, with evolution of nitrous gas. — 5. In alkaline solution, it is converted by *hydrosulphuric acid,* first into rubiacin, and then into rubiafin. — 6. Not altered by boiling with *chromate of potash* and sulphuric acid.

Combinations. Rubiacic acid dissolves slightly in boiling *water,* colouring it yellow.

It dissolves in aqueous *ferric chloride,* and is precipitated therefrom in flocks by acids.

With bases it forms the *rubiacates* = $C^{32}MH^8O^{17}$, according to

E 2

Schunck. Aqueous rubiacate of potash forms with *chloride of barium* a yellow precipitate; with *chloride of calcium*, orange-coloured crystalline; with *alum*, yellow; with *neutral acetate of lead*, red; with *ferrous sulphate*, greenish-grey. With *ferric chloride* it forms a red-brown liquid and a scanty precipitate of the same colour. It precipitates *cupric sulphate* dark-red; *mercurous nitrate* yellow; *mercuric nitrate*, yellow and crystalline; *stannous chloride*, dirty yellow; *stannic chloride*, light yellow. From an acid solution of *auric chloride* it throws down a yellow precipitate, which is not altered by boiling, and dissolves with purple colour in potash.

Rubiacate of Potash. — *Preparation*, p. 51. — Needles or prisms having a light brick-red colour and silky lustre. Detonates when heated. If contaminated (or combined, *vid. inf.*) with rubiacin, it is granular, has less silky lustre, and detonates less strongly. — It dissolves in water with red colour, changing to purple by the action of potash-ley. With alcohol it forms a blood-red, transparent solution.

					Schunck. mean.
32	C	192·0	51·17		51·37
8	H	8·0	2·13		2·41
16	O	128·0	34·12		33·18
	KO	47·2	12·58		13·04
$C^{32}H^8KO^{17}$		375·2	100·00		100·00

Rubiacate of Silver. — Obtained by precipitating the potash-salt with nitrate of silver. — Yellow or faintly orange-coloured precipitate. Cinnabar-red if mixed or combined with rubiacin.

					Schunck.
32	C	192	43·24		43·63
8	H	8	1·80		2·40
16	O	128	28·83		
	AgO	116	26·13		
$C^{32}H^8AgO^{17}$		444	100·00		

Rubiacic acid dissolves sparingly in boiling *alcohol*, forming a yellow solution. This solution, which deposits nothing on cooling, becomes iridiscent and yields small crystals when mixed with water. The aqueous or alcoholic solution imparts a faint colour to mordanted fabrics.

With Rubiacin? If rubiacic acid prepared from madder-liquor (p. 51) has not been boiled thoroughly, or not sufficiently, with alcohol, it remains contaminated with rubiacin, which then passes also into the rubiacates, so that the acid thus obtained may be regarded either as a mixture or as a compound of the two bodies in equivalent proportions. — It reacts like rubiacic acid, but when heated between two watch-glasses, yields a large quantity of yellow sublimate, probably consisting of rubiacin, and forms, with potash, a granular salt having less silky lustre, a dark red colour, and yielding with aqueous nitrate of silver a shining cinnabar-red precipitate, not altered by light or by the action of boiling water.

Acid, precipitated from the Potash-salt.				Schunck.
64 C	 384	....	61·93 ..	61·19
20 H	 20	.... .	3·22	... . 3·55
27 O	 216	....	34·85 .	.... 35·26

$C^{32}H^9O^{17},C^{32}H^{11}O^{10}$ .... 620 .. .... 100·00 .. .... 100·00

Silver-salt, precipitated from the Potash-salt.				Schunck.
64 C	 384	.. ....	46·04	.... 46·08
18 H	 18	......	2·15	.... 2·20
25 O	 200	....	24·00	... . 24·37
2AgO	 232	.... .	27·81 .	27·35

$C^{64}H^{18}Ag^2O^{27}$ .... 834 .... 100·00 .. .. 100·00

4. Rubiadin.

$$C^{32}H^{13}O^9.$$

Ed. Schunck (1853). *N. Phil. Mag.* 5, 410 and 495; *J. pr. Chem.* 59, 453. — *N. Phil. Mag.* 12, 200 and 270; *J. pr. Chem.* 70, 154.

Formation. 1. In the decomposition of rubian by fixed alkalis (p. 36); sometimes also in the decomposition of rubian by bicarbonate of baryta (p. 39). — 2. In the decomposition of rubihydran or rubide-hydran by dilute hydrochloric or sulphuric acid (pp. 44, 45), sugar being always formed at the same time.

Preparation. 1. From the mother-liquor obtained in the decomposition of rubian by alkalis (xiv, 134) after separation of the compound of alizarin and alumina. This mother-liquor, mixed with dilute sulphuric acid and a large quantity of water, deposits yellow flocks containing rubiretin, verantin, and rubiadin, while sugar remains in solution. These flocks are collected, washed, and dissolved in boiling alcohol, and the solution is mixed with acetate of lead, which throws down rubiretin and verantin as a brownish-purple precipitate (see *Rubiretin*), while rubiadin remains in solution, still mixed however with a small quantity of rubiretin. By precipitating the solution with a large quantity of water, dissolving the yellow flocks thereby obtained in the exact quantity of boiling alcohol required, and digesting with hydrate of lead (or stannous hydrate), the rubiretin is removed, and the hot-filtered solution deposits rubiadin on cooling; an additional quantity of that substance, but in an impure state, is obtained by evaporating the mother-liquor. This latter product may be purified by sublimation. — 2. An aqueous solution of rubihydran (p. 44) is boiled with hydrochloric or sulphuric acid till it becomes colourless, and no longer deposits yellow flocks or a brown resin. These flocks are a mixture of rubiretin, verantin, and rubiadin, with a small quantity of alizarin; the alizarin may be separated by acetate of alumina, and then the rubiadin in the same manner as from the mixture of these bodies obtained by the first method.

Properties. Golden-yellow, sometimes rectangular tables, yellow or orange-coloured needles, resembling rubianin. When slightly contaminated with foreign substances, it is obtained as a granular mass or a yellow amorphous powder. By careful heating between two watch-glasses, it may be sublimed in yellow or orange-coloured, shining, micaceous laminæ, leaving only a small quantity of charcoal.

									Schunck.	
								earlier	later
	Calculation according to Schunck.							*at* 100°.	*mean.*
	earlier.				*later.*				
32 C	192	....	71·64	32 C	192	....	69·31	.... 71·22	.... 69·61
12 H	12	....	4·47	13 H	13	....	4·69	.... 4·83	.... 5·06
8 O	64	....	23·89	9 O	72	....	26·00	.... 23·95	.... 25·33
$C^{32}H^{12}O^{8}$....	268	....	100·00	$C^{32}H^{13}O^{9}$.... 277		....	100·00	.... 100·00	.... 100·00

The earlier and later formulæ proposed by Schunck differ from one another by 1 at. water.

Decompositions. 1. *Heated* on platinum-foil, it melts and burns with flame.— 2. It dissolves in cold *oil of vitriol* with deep yellow colour, and is precipitated unchanged by water; in hot oil of vitriol it dissolves with dark brownish-yellow colour, eliminating a small quantity of sulphurous acid, and yields with water a yellow-brown precipitate. — 3. Gives off red fumes when boiled with *nitric acid.*— 4. With *alkalis* it behaves like rubianin.— 5. It is but slightly altered by *ferric chloride.*

Combinations. Insoluble in *water,* even at the boiling heat. By aqueous *ammonia* and *carbonate of soda* it is not dissolved in the cold, but dissolves with blood-red colour at the boiling heat. The ammoniacal solution gives off ammonia in contact with the air, and deposits rubiadin in the form of yellow films. With *chloride of barium* it is first decolorised and then forms dark brownish-red needles; with *chloride of calcium* it forms a light-red precipitate. An alcoholic solution of rubiadin does not precipitate *acetate of lead;* with *cupric acetate* it first forms a darker-coloured liquid, and then a dark brown-red precipitate. It is insoluble in aqueous *ferric chloride.*

Dissolves in *alcohol* more easily than rubianin.

5. Rubiagin.

$$C^{32}H^{14}O^{10} \text{ or } C^{44}H^{17}O^{13}.$$
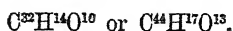
Ed. Schunck. *J. pr. Chem.* 59, 471.

Formation. In the fermentation of madder and by the action of erythrozym on rubian, together with many other products (xiv, 134 and xvi, 37).

Preparation. When the alcoholic filtrate obtained by the fermentation of madder (xiv, 134) after precipitation of alizarin, verantin, rubiretin, and rubiafin, with acetate of lead, is mixed with a large

quantity of water, a faintly orange-coloured precipitate is formed, consisting of the lead-compounds of rubiagin and rubiadipin; this precipitate is to be collected and decomposed by boiling dilute sulphuric acid. The undissolved portion washed with water, then boiled with alcohol, yields to the latter rubiagin and rubiadipin, both of which remain, after evaporation of the alcohol, as a soft, dark-brown fatty mass, and may be separated by cold alcohol, which dissolves chiefly the rubiadipin; the undissolved rubiagin may be purified by recrystallisation from hot alcohol.

Properties . Small lemon-yellow, spherical granules, or small concentrically grouped needles.

												Schunck.
32 C	....	192	....	67·12		44 C	....	264	. .	68·57	....	68·10
14 H	....	14	....	4·89		17 H	....	17	....	4·41		5·14
10 O	....	80	....	27·99		13 O	....	104	...	27·02		26·76
$C^{32}H^{14}O^{10}$....		286	....	100·00		$C^{44}H^{17}O^{13}$....		385	....	100·00		100·00

Schunck is undecided between the preceding formulæ, either of which he regards as capable of explaining the production of rubiagin from rubian ; either $C^{56}H^{34}O^{30}$ + 4HO = $C^{32}H^{14}O^{10}$ + $2C^{12}H^{12}O^{12}$, or $C^{56}H^{34}O^{30}$ = $C^{44}H^{17}O^{13}$ + $C^{12}H^{12}O^{12}$ + 5HO.

Decompositions. 1. Does not sublime without decomposition, but when heated in a test-tube it yields a slight crystalline deposit and drops of oil. —2. When heated on platinum-foil it melts and burns with flame, leaving a difficultly combustible coal. — 3. In cold *oil of vitriol* it dissolves with dark red-brown colour, in hot oil of vitriol with black colour, eliminating a large quantity of sulphurous acid. — 4. Dissolves in boiling *nitric acid* with evolution of nitrous gas, forming a yellow liquid which yields shining crystals as it cools.

Combinations. Insoluble in boiling *water*. In *ammonia* it dissolves with blood-red colour, but slowly, and only at the boiling heat; on evaporating the liquid, the whole of the ammonia is given off, and rubiagin remains in yellow crystals. It dissolves easily in *soda-ley*, and is precipitated in yellow flocks by acids; in *baryta* and *lime-water* with blood-red colour, precipitable by carbonic acid. From the ammoniacal solution it is but slightly precipitated by *chloride of barium* and *chloride of calcium*.

Lead-compound of Rubiagin. An alcoholic solution of rubiagin gives no precipitate at first with neutral acetate of lead, but turns yellow, and then throws down orange-coloured grains, which dissolve sparingly in boiling alcohol, easily in an alcoholic solution of neutral acetate of lead. This property distinguishes rubiagin from rubiacin, rubiadin and rubiafin.

											Schunck.
32 C	....	192	....	30·91	44 C	....	264	....	31·73	....	31·29
14 H	....	14	....	2·25	17 H	....	17	....	2·04	....	2·67
10 O	....	80	....	12·89	13 O	....	104	....	12·53	....	12·60
3 PbO	. ...	336	....	53·95	4 PbO	....	448	....	53·70	....	53·44
$C^{32}H^{14}O^{10}$,3PbO ...		622	....	100·00	$C^{44}H^{17}O^{13}$,4PbO ..		833	..	100·00	....	100·00

Rubiagin boiled with *ferric chloride* assumes a darker colour, but not deep purple-brown like rubiafin and rubiacin. The hot-filtered

solution deposits, on cooling, yellow laminæ, probably of rubiagin, and is then no longer precipitated by hydrochloric acid. No rubiacic acid is formed in this reaction.

An alcoholic solution of rubiagin mixed with *cupric acetate* first assumes a brownish-yellow colour, and then yields an orange-coloured precipitate.

Rubiagin dissolves in boiling alcohol more easily than rubianin or rubiadin; in boiling *acetic acid* it dissolves with yellow colour, and crystallises on cooling. (Does not crystallise? *Zeitschr. Ch. Pharm.* 3, 162.)

6. Rubianin.

$C^{32}H^{19}O^{15}$.
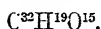
Ed. Schunck (1851). *N. Phil. Mag. J.* 3, 213 and 354; *Ann. Pharm.* 81, 151; *Chem. Soc. Qu. J.* 12, 213.

Formation. By boiling rubian with acids (p. 36).

Preparation. (xiv, 134.)

Properties. Lemon-yellow needles, having a silky lustre, lighter in colour than rubiacin.

								Schunck. at 100° (*mean*).
32	C	. ...	192	....	58·00	.. ..	57·59
19	H	....	19	....	5·74	....	5·42
15	O	....	120	....	36·26	... .	36·99
$C^{32}H^{19}O^{15}$		....	331	....	100·00	....	100·00

Schunck appears to prefer this formula to those which which were formerly regarded as probable (*J. pr. Chem.* 61, 66). Gerhardt suggested the formula $C^{26}H^{10}O^{10}$ (calc. 57·14 p.c. C., 4·76 H., 38·10 O) = alizarin + 4aq. (*Traité* 3, 493). Shunck afterwards gave the formula $C^{44}H^{24}O^{20}$, which however does not agree so well with his analysis (calc. 58·93 p.c. C., 5·33 H).

Heated on platinum-foil it melts to a brown liquid, chars and burns. — Heated in a test-tube, it yields a smaller quantity of crystalline sublimate than rubiacin, and leaves a large quantity of charcoal. — Dissolves with yellow colour in cold *oil of vitriol*, and is carbonised by hot oil of vitriol, with evolution of sulphurous acid. — *Chlorine* converts it into perchlororubian (? *Zeitchr. Ch. Pharm.* 3, 161).

More soluble in boiling *water* than rubiacin. Dissolves without decomposition in *nitric acid*, even when hot and concentrated. Insoluble in the cold in *ammonia, carbonate of potash*, and *carbonate of soda*, but dissolves at the boiling heat, forming a blood-red solution, whence it crystallises after standing for some time. — The ammoniacal solution forms red precipitates with *chloride of barium* and *chloride of calcium*. The alcoholic solution does not precipitate *neutral acetate of lead*. Rubianin dissolves with dark-brown colour in a strong solution of *ferric chloride*, without forming rubiacic acid.

Rubianin is less soluble in *alcohol* than rubiretin and verantin. Dyes mordanted fabrics but faintly.

7. Rubiretin.

$C^{14}H^6O^4$.

ED. SCHUNCK. See Memoirs cited under Rubian (p. 32).

Alpha-resin.

Occurrence. In madder root (Schunck). Produced (as well as verantin), according to Higgin, when the root is boiled with water, — according to Wolff and Strecker, perhaps from purpurin (xiii, 325) by the action of alkalis.

Formation. Together with many other products, when rubian, rubihydran, or rubidehydran, is boiled with acids or with alkalis ; by the action of erythrozym (p. 37), air and warmth (p. 36) on rubian, and by boiling chlororubian with alkalis (p. 47).

Preparation. Rubiretin is obtained as a bye-product in the preparation 1 of rubian (p. 33); in the preparation 1 (xiv, 133) and 3 (xiv, 135) of alizarin, and in the preparation 1 of rubiacin (xvi, 48; xiv, 136); in the last case as a lead-compound.
The mixture of the lead-compounds of rubiretin and verantin obtained by the last-mentioned process, yields, when decomposed by boiling hydrochloric acid, a brown powder, from which the rubiretin may be dissolved out by cold alcohol, the greater part of the verantin remaining behind. The alcoholic solution, when evaporated, leaves the rubiretin, which, if it does not melt in boiling water, must be purified by re-solution in cold alcohol and evaporation of the filtrate. A similar mode of purifying may be applied to rubiretin obtained as a secondary product under other circumstances.

Properties. Dark reddish brown resin, brittle and friable ·in the cold, soft at 65°. Melts, at about 100°, to dark brown drops.

				Schunck.		*mean.*
14 C	....	84	....	68 85	....	68·41
6 H	....	6	....	4·91	....	5·22
4 O	....	32	....	26·24	....	26·37
$C^{14}H^6O^4$	....	122	....	100·00	....	100·00

Isomeric with benzoic acid.

Decompositions. 1. Heated in a test-tube, it generally yields a scanty sublimate of alizarin, together with a brown oil. — 2. It is decomposed by hot *oil of vitriol.* — 3. Boiling *nitric acid* converts it into a yellow substance, which no longer softens in boiling water, and is scarcely soluble in alcohol. — 4. *Chlorine* passed into the alcoholic solution of rubiretin, decolorises it, and renders it no longer precipitable by acids.

Combinations. Rubiretin dissolves sparingly in boiling *water*, but softens therein, and on cooling deposits yellow flocks, which increase on the addition of an acid. It dissolves with dark orange colour in *oil of vitriol*, and is precipitated by water. It dissolves in *ammonia*, in the *caustic fixed alkalis* and their *carbonates*, forming brown-red solutions, from which it is precipitated by acids. The ammoniacal solution forms purple precipitates with *chloride of barium* and *chloride of calcium*, dirty red with *alum* and *nitrate of silver*. It dissolves in aqueous *ferric chloride*, with dark red-brown colour, and is precipitated by acids.

Easily soluble in cold *alcohol*. When free from alizarin, it does not dye mordanted fabrics.

8. Verantin.

$$C^{14}H^5O^5.$$

Ed. Schunck.   See Memoirs cited under Rubian (p. 32).

Beta-resin.

Occurrence.   In madder-root.

Formation.   Produced, together with many other products, when rubian, rubihydran or rubidehydran is boiled with acids or alkalis; by the action of erythrozym on rubian (p. 37); and by boiling chlororubian with alkalis (p. 47).

Preparation.   The first mode of preparing alizarin from rubian (xiv, 133), and the first mode of preparing rubiadin (p. 53), yield pure verantin as a secondary product.

In the first mode of preparing rubian, verantin is obtained partly pure (xiv, 134), partly in combination with ferric oxide. This compound is freed from iron by hydrochloric acid, then washed and dissolved in boiling alcohol, which, on cooling, deposits verantin in the form of a brown powder.

By the third method of preparing alizarin from rubian (xiv, 135), lakes are obtained, composed of alizarin and verantin in combination with stannous oxide, the greater part of which oxide may be removed by hydrochloric acid. The dark red-brown residue is washed with hydrochloric acid, then with water, and dissolved in boiling alcohol, which takes up all but the undecomposed compound of verantin and stannous oxide; the solution deposits verantin on cooling, and when further evaporated, leaves a mixture of verantin and alizarin.

Debus (*Ann. Pharm.* 66, 354) found that when the colouring matters of madder, precipitated by zinc-oxide in the preparation of purpurin, and separated from the zinc-oxide, were dissolved in ether, a brown resin remained, which, when dissolved in boiling alcohol, separated partly on cooling, partly after evaporation of the alcohol, and contained on the average 65.1 p.c. carbon, 5.99 hydrogen and 28.91 oxygen, whence Debus deduces the formula $C^{60}H^{33}O^{20}$ (calc. 65.09 p.c. C., 5.95 H. and 28.96 O.). This substance agrees with verantin in its behaviour to alcohol.

Properties.   Reddish brown amorphous powder, resembling snuff or

roasted coffee. In boiling water it scarcely melts, but becomes soft and coherent. The alcoholic solution reddens litmus.

				Schunck.
				mean.
14 C	84	....	65·11	65·73
5 H	5	....	3·87	4·13
5 O	40	....	31·02	30·14
$C^{14}H^5O^5$	129	....	100·00	100·00

According to Gerhardt, it is perhaps $C^{40}H^{14}O^{14}$ (calc. 65·57 C., 3·82 H., 30·61 O.) = 2 at. alizarin + 2 at. aq. (*Traité*, 3, 423.)

Decompositions. 1. Heated in a test tube, it yields an oily distillate without any trace of crystals. — 2. On platinum-foil it burns without residue. — 3. Cold *oil of vitriol* dissolves it with brown colour; by hot oil of vitriol it is carbonised, with evolution of sulphurous acid. — 4. It is insoluble in dilute *nitric acid,* but the strong acid dissolves it on boiling, with yellow colour, and evolution of nitrous gas. — Its alkaline solution is decolorised by *chlorine.*

Combinations. It is nearly insoluble in boiling *water.* It dissolves in *ammonia,* and remains, on evaporation, as a brown film, free from ammonia ; in the *fixed alkalis* and their *carbonates,* it dissolves with dingy red colour, and is precipitated in brown flocks by acids.

Barium-compound. Obtained by precipitating the ammoniacal solution of verantin with chloride of barium.

				Schunck.
42 C	252	....	48·27	48·57
13 H	13	....	2·49	3·15
13 O	104	....	19·93	18·59
2 BaO	153	....	29·31	29·69
$2(C^{14}H^4O^4,BaO) + C^{14}H^5O^5$	522	....	100·00	100·00

The alcoholic solution of verantin forms a dark brown precipitate with *neutral acetate of lead.*

Cupric Compound. Alcoholic verantin precipitates cupric acetate. The precipitate varies in composition, even when obtained by the same mode of preparation.

				Schunck.
				at 100°.
14 C	84	....	52·5	52·24
4 H	4	....	2·5	3·10
4 O	32	....	20·0	19·19
CuO	40	....	25·0	25·47
$C^{14}H^4O^4CuO$	160	....	100·0	100·00

				Schunck.
56 C	336	....	55·17	55·54
17 H	17	....	2·79	3·41
17 O	136	....	22·34	21·53
3 CuO	120	....	19·70	19·52
$3(C^{14}H^4O^4,CuO)C^{14}H^5O^5$	609	....	100·00	100·00

Stannous compound. — Preparation (p. 58). The compound obtained as above is dissolved in carbonate of soda, filtered from a small quantity of zinc-oxide, and precipitated by an acid. Dark brown flocks, forming when dry a shining, black, coherent mass. It cannot be resolved into its constituents, inasmuch as it dissolves in ammonia and in the fixed alkalis and their carbonates, and is precipitated undecomposed by acids, and its solution in caustic soda, after hydrosulphuric acid gas has been passed through it, yields with acids a precipitate from which boiling alcohol does not extract anything soluble.

	Calculation according to Schunck.	Schunck. *at* 100° ; *mean.*
56 C	29·76	29·96
36 H	3·18	3·31
36 O	25·52	25·35
7 SnO	41.54	41·38
$4C^{14}H^5O^5,7SnO + 16Aq.$	100·00	100·00

Verantin dissolves readily in boiling *alcohol,* and separates in the pulverulent form on cooling. It does not impart any colour to mordanted fabrics.

With Alizarin ?—Alizarin and verantin, though each by itself is perfectly insoluble in a boiling solution of alum, nevertheless dissolve in it when present together, forming a carmine-red liquid of the colour of purpurin. Since, also, according to Debus, the composition of purpurin agrees with that of a mixture of 1 at. alizarin ($C^{14}H^5O^4$, according to Schunck), and 3 at. verantin,—or, according to another preparation, with that of 3 at. alizarin and 1 at. verantin, Schunck formerly regarded purpurin as a mixture of alizarin and verantin in varying proportions, and as decomposible into the two (xiii, 325); more recently, however (*Chem. Soc. Qu. J.* xii, 217), he admits the independent existence of purpurin.

9. Rubiadipin.

$C^{30}H^{24}O^5$?
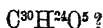
Ed. Schunck. *J. pr. Chem.* 59, 474.

Formation. By the fermentation of rubian (p. 37).

Preparation (p. 55).

Properties. Semifluid, yellowish brown fat. Does not become hard and friable, even when heated for a long time. Melts in boiling water to oil drops, which rise to the surface.

Decompositions 1. When heated on platinum-foil, it burns with a bright flame, leaving charcoal. — 2. Heated in a test-tube, it gives off acrid fumes like fat.—3. It is carbonised by *oil of vitriol.*— 4. Scarcely altered by boiling *nitric acid.*

Combinations. Insoluble in *water.* It dissolves in alkalis with blood-red colour, forming a liquid, which froths like soap-solution. Its ammoniacal solution forms a slight precipitate with *chloride of barium.* The alcoholic solution does not precipitate *cupric acetate.*

Lead-compound. — Alcoholic rubiadipin forms with neutral acetate of lead, a pale reddish brown precipitate, insoluble in boiling alcohol, easily soluble in alcoholic neutral acetate of lead, forming a brown-red solution from which it is precipitated by water.

					Schunck.
30	C	180	......	50·60	...... 50·89
24	H	24	....	6·74	.... 6·93
5	O	40	....	11·26	.... 10·83
	PbO	112	....	31·40	..... 31·35
$C^{30}H^{24}O^5,PbO$		356	....	100·00	.... 100·00

10. Oxyrubian.

$$C^{44}H^{14}O^{12}.$$
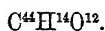
Ed. Schunck. *J. pr. Chem.* 70, 176.

Formation and Preparation (p. 47). The dark, brown-red flocks prepared on boiling chloro-rubian with caustic soda, are coloured yellowish brown by boiling hydrochloric acid, may be washed with boiling alcohol, and if then dried, yield oxyrubian as a yellowish brown powder, which, if free from chlorine, yields, when heated in a test-tube, a yellow crystalline sublimate, easily soluble in alkalis, not altered by hydrosulphate of ammonia, but turned red-brown by alkalis.

Calculation according to Schunck.				Schunck.
				mean.
44 C	264	....	70·58	.... 70·71
14 H	14	....	3·74	.... 3·92
12 O	96	.. ....	25·68	... .. 25·37
$C^{44}H^{14}O^{12}$	374	....	100·00	.... 100·00

Schunck is undecided between the formula just given and $C^{32}H^{10}O^8$ or $C^{32}H^{11}O^9$, and accordingly as to the manner in which the formation of oxyrubian takes place, viz., $C^{44}ClH^7O^{24} + NaO = C^{44}H^{11}O^{12} + NaCl + 13HO$, or $= C^{32}H^{10}O^8 + C^{12}H^{12}O^{12} + NaCl + 5HO$.

11. Perchlororubian.

$$C^{44}Cl^9H^9O^5.$$
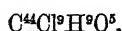
Ed. Schunck. *J. pr. Chem.* 70, 178; *N. Phil. Mag. J.* 12, 200, and 270.

Formation and Preparation. When finely pulverised chlororubian is covered with water, and treated with chlorine till the space above the

liquid becomes filled with the gas, the chlorine is gradually absorbed, more quickly on agitation, and the chlororubian is converted into a white powder, which must be washed with water and recrystallised from boiling alcohol, if necessary with help of animal charcoal. — Perchlororubian is likewise obtained, though in a less pure state, by the continued action of chlorine on rubian.

Properties. Colourless, transparent, four-sided tables, with splendid iridescence. When cautiously heated, it sublimes completely in micaceous scales. Neutral.

	Calculation according to Schunck.				Schunck. mean.
44 C	....	264·0	....	37·09	.... 37·05
9 Cl	....	319·5	....	44·77	.... 44·40
9 H	....	9·0	....	1·26	.... 1·51
15 O	... .	120·0	. ...	16·88	.... 17·04
$C^{44}Cl^9H^9O^{15}$	....	712·5	....	100·00	.... 100·00

Decompositions. 1. When introduced into a red-hot tube, it detonates, and gives off acid vapours, with little or no crystalline sublimate. — 2. When heated on platinum-foil, it melts to a brown mass, and burns with a smoky, green-edged flame, leaving but little charcoal.— 3. Dissolves easily in boiling *hydrosulphate of ammonia*, and the solution after supersaturation with nitric acid, is precipitated by silver-salts.

Combinations. Insoluble in *water*. Dissolves in warm *oil of vitriol*, and at the boiling heat colours that liquid black, and escapes in vapours which condense in the crystalline form. Insoluble in boiling *nitric acid* of sp. gr. 1·37, but dissolves in the same acid of sp. gr. 1·52 and is precipitated unchanged by water. Does not dissolve in *ammonia* or in strong boiling soda-ley. The alcoholic solution is not precipitated by alcoholic *neutral acetate of lead.*
Soluble in *alcohol* and in *ether*.

12. Chlororubiadin.

$$C^{32}ClH^{12}O^9.$$

Ed. Schunck.   *J. pr. Chem.* 70, 171.

Formation and Preparation (p. 47). Chlororubian is dissolved in dilute hydrochloric or sulphuric acid at the boiling heat, and boiled till the solution, which is at first clear and yellow, becomes milky and deposits yellow flocks, which may be washed with water and crystallised from boiling alcohol.

Properties. Broad shining yellow needles or laminæ. The alcoholic solution reddens litmus.

Calculation *according to* Schunck.				Schunck. *at* 100°.		
32 C	192·0	....	61·65	.... 60·56	to	61·67
Cl	35·5	....	11·36	.... 11·21	„	10·95
12 H	12·0	....	3·85	.... 4·23	„	4·26
9 O	72·0	....	23·14	.... 24·00	„	23·12
$C^{32}H^{12}ClO^9$	311·5	......	100·00	...... 100·00		100·00

Decompositions. 1. Heated in a test-tube, it melts, gives off pungent vapours smelling like hydrochloric acid, and yields, first oil, then a crystalline sublimate. — 2. On platinum-foil it burns with a yellow, green-edged flame, and leaves a large quantity of charcoal. — 3. The orange-red solution of chlororubiadin in *oil of vitriol* becomes purple-red on boiling, and gives off a small quantity of sulphurous acid, together with a crystalline sublimate, which coats the sides of the vessel. — 4. When chlororubiadin suspended in water is treated with *chlorine gas*, it acquires a lighter colour, and is converted into a peculiar substance which when dissolved in alcohol, remains, after the spontaneous evaporation of the liquid, as a transparent dark yellow soft mass (hard, after evaporation over the water-bath). This mass contains 46·55 p. c. C., 3·12 H. and 30·42 Cl., melts when heated in a test-tube, and gives off acid vapours, together with an oily distillate, which afterwards solidifies partially in the crystalline form. It dissolves in caustic soda as well as in oil of vitriol, in the latter with brown colour, and without evolution of sulphurous acid, even at the boiling heat. It is not precipitated from its aqueous solution by nitrate of silver. — 5. Chlororubiadin forms with *nitric acid* of sp. gr. 1·52 (weaker acid does not attack it) an orange-coloured solution, which gives off red vapours at the boiling heat, and is afterwards precipitated by nitrate of silver; before boiling, it is not precipitated by that reagent. — 6. Dissolves in *caustic soda*, with purple colour, and after boiling for some time, deposits reddish-brown flocks, which become orange-coloured in boiling hydrochloric acid, are insoluble in boiling alcohol after washing and drying, and have the appearance of oxyrubian, but consist of 65·12 p. c. C., 3·26 H., 9·36 Cl., and 22·26 O. — 7. With aqueous *hydrosulphate of ammonia* it forms a solution which is red at first, but afterwards becomes purple, and finally brown-red From the purple solution, nitric acid throws down orange-coloured flocks. free from sulphur and chlorine, partially soluble in alcohol, perfectly soluble in boiling nitric acid, and separating therefrom, after a while. in long sword-shaped crystals. — 8. Chlororubiadin throws down metallic gold from an alcoholic solution of *auric chloride.*

Combinations. Chlororubiadin is insoluble in water. It dissolves in cold *oil of vitriol*, and in *nitric acid* of sp. gr. 1·52, and is precipitated unchanged by water (vid. sup.). It dissolves in aqueous *ammonia*, the solution giving off all its ammonia when left to evaporate.

It dissolves in *caustic soda* with purple, and in *alkaline carbonates* with blood-red colour.

Barium-compound. — When an ammoniacal solution of chlororubiadin is mixed with chloride of barium, filtered from the flocks which fall down, and the filtrate left to stand in a vessel which protects it from the air, long red needles are obtained, which may be washed with water and dried in vacuo. The compound gives off 8·24 p. c. water

at 100°, and then contains 51·52 p. c. C., 3·44 H., and 15·65 BaO, whence Schunck deduces the formula 3 BaO,C³²ClH¹²O⁹.

Calcium-compound. — Chlororubiadin dissolved in ammonia throws down from chloride of calcium, after a while, a dark red amorphous powder, the liquid at the same time becoming decolorised.

Alcoholic chlororubiadin does not precipitate *acetate of alumina,* or *acetate of lead,* even on addition of ammonia; *ferric acetate* is likewise not precipitated by it. From its solution in alcohol it is precipitated, after some time, with light brown colour, by *cupric acetate.*

Chlororubiadin is soluble in *alcohol.*

13. Erythrozym.

HIGGIN. *Phil. Mag. J.* 33, 282; *J. pr. Chem.* 46, 1.
ED. SCHUNCK. *N. Phil. Mag. J.* 5, 410 and 495; *J. pr. Chem.* 59, 460.

The peculiar nitrogenous matter of madder-root.

Preparation. When a pound of madder, placed on a calico filter, is rinsed with 4 quarts of water at 38°, — the infusion mixed with an equal quantity of alcohol,—and the precipitated dark red flocks are collected, boiled with alcohol till everything soluble therein is removed, washed with cold water as long as the liquid which runs off gives a precipitate with neutral acetate of lead, and then dried over the water-bath, — *erythrozym a* is obtained, which, in the moist state, is a dark brown-red granular mass, like coagulated casein, and when dry, forms black hard lumps, difficult to pulverise. When this product is used for the decomposition of rubian (p. 37), and then treated successively with cold water and boiling alcohol, *erythrozym b* remains behind. — When an infusion of madder prepared with warm water is precipitated with tartaric acid, the precipitate washed with water, with boiling alcohol, then again with cold water, and dried, *erythrozym c* is obtained. — Erythrozym *a* covered with water till it begins to evolve gas and emit an odour which indicates decomposition, then boiled with alcohol, and dried, leaves *erythrozym d* (Schunck).

Calculations according to Schunck.

a.			Schunck.	b.			Schunck.
52 C		40·48	41·07	52 C		44·82	44·99
34 H		4·09	4·45	32 H		4·59	4·62
2 N		3·37	3·26	2 N		4·02	4·11
40 O		38·57	37·64	30 O		34·51	34·98
4 CaO		13·49	13·58	3 CaO		12·06	11·30
C⁵⁶H³⁴N²O⁴⁰,4CaO		100·00	100·00	C⁵²H³²N²O³⁰,3CaO		100·00	100·00

c.			Schunck.	d.			Schunck.
52 C		48·00	47·68	52 C		46·60	45·65
30 H		4·61	4·61	28½ H		4·25	4·22
2 N		4·30		1½ N		3·13	3·22
28 O		34·48		28 O		33·48	33·40
2 CaO		8·61	8·32	3 CaO		12·54	13·51
C⁵²H³⁰N²O²⁸,2CaO		100·00		C⁵²H²⁸·⁵N¹·⁵O²⁸,3CaO	100·00		100·00

Hence it would appear that a = (Rubian) $C^{56}H^{34}O^{30}$ + $2NO^5$ + $4CaO$; $b = a -$ $(2HO,4CO^2,CaO)$; $c = b - (2HO,CaO)$; $d = 2a - (8CO^2,8HO,NH^3,CaO)$ (Schunck).

The following observations apply to erythrozym a. — When *heated* on platinum-foil it emits an odour of burning horn, burns without much flame, leaves charcoal, and finally carbonate of lime. By prolonged *immersion in water*, it is decomposed, giving off gases, and an unpleasant but not putrid odour, turns red, assumes a flocculent character, and is converted into an acid. By this change, its power of decomposing rubian is increased at first, then diminished. With *water*, it forms a muddy red-brown liquid, but does not appear to dissolve, inasmuch as the filtrate does not decompose solution of rubian. By boiling with water, it is coagulated and separates from the red liquid in dingy red flocks. A similar action is exerted by alcohol and salts. By acids, it is converted, with loss of lime, into yellow-brown flocks, which, after being washed, no longer form a mud with water, and dissolve in alcohol to a turbid, pale purple liquid, which gives off ammonia when boiled. It is carbonised by heating with *oil of vitriol*, and decomposed by *nitric acid*. — Decomposes rubian and rubianic acid in the manner already described (pp. 37, 40) (Schunck).

Higgin obtained the nitrogenous constituent of madder—to which he attributes the power of converting his xanthin into rubiacin and alizarin (xiv, 130),—in an impure and partially altered state, by subjecting madder mixed to a pulp with water to strong pressure, precipitating the liquid with a large quantity of alcohol, and washing the precipitated flocks with alcohol. There then remained a brown nitrogenous matter, which, when heated, emitted an empyreumatic ethereal odour, and left a large quantity of ash, but probably contained much pectin and woody fibre. This substance is insoluble in water; emits the peculiar odour of protein bodies when heated with hydrate of soda; forms with nitric acid a yellow mass which is reddened by ammonia,—whereupon acids throw down a yellow powder of xanthoproteic acid,—and dissolves readily in dilute alkalis; it is, therefore, probably a protein-substance.

14. Chlorogenin.

ED. SCHUNCK. See memoirs cited under Rubian (p. 32), 1 and 3.

The substance contained in the aqueous extract of madder, which turns green when boiled with acids; it has not yet been obtained in the pure state. — According to Schunck, it is a constituent of the xanthin of Higgin and of Kuhlmann — the *madder-yellow* of Runge — and imparts to this body the property of turning green when boiled with acids. (But does Runge's madder-yellow possess this property? Kr.) It appears to be identical with Rochleder's *rubichloric acid*, and with Runge's *Rubiaceensäure* (*Pogg.* 31, 521). Kr.

It remains, together with sugar and ash-constituents, in the liquid obtained in the preparation of rubian (p. 33), and filtered from the precipitate formed by acids.

When the decoction of madder, obtained as described on page 33, is precipitated by oxalic acid, and the filtrate neutralised with lime,

the liquid, if again filtered and evaporated over the water-bath, becomes coloured, and ultimately leaves a thick dark brown syrup, which dissolves in water with the exception of some brown decomposition-products formed during the evaporation. The solution has an acid reaction arising from the presence of phosphoric acid, and turns green when boiled with acids. The solution precipitated with basic acetate of lead, filtered from the precipitate, freed from excess of lead by hydrosulphuric acid, and evaporated over oil of vitriol, after filtration, leaves a brownish yellow, honey-like residue which does not dry up again. This is chlorogenin mixed with the small quantity of sugar existing ready-formed in the madder, and with the acetates of potash, lime and magnesia.

Thick yellow or brown syrup, which absorbs water from the air. It has a disagreeable taste, both sweet and bitter. Its aqueous solution deposits a brown powder during evaporation. When heated, it swells up, gives off an odour of acetone, and when burnt, leaves a mixture of the carbonates of potash, lime and magnesia. When boiled with dilute *hydrochloric* or *sulphuric acid*, it emits a repulsive odour, turns dark green, and deposits a dark green powder (see *Chlororubin*). When treated with *caustic potash*, it turns brown, and then gives off a small quantity of ammonia on boiling. It is not precipitated by *saline solutions*, unless it undergoes decomposition.

Soluble in *alcohol*, insoluble in *ether*. Does not colour mordanted fabrics, unless it has been altered by the action of the air, in which case it imparts a brown colour to stuffs mordanted with alumina or iron (Schunck).

Appendix to Chlorogenin.

a, Rubichloric Acid.

ROCHLEDER. *Wien. Akad. Ber.* 6, 433; *Ann. Pharm.* 80, 327; *J. pr. Chem.* 55, 385.

R. SCHWARZ. *Wien. Akad. Ber.* 6, 446; *Ann. Pharm.* 80, 333; *J. pr. Chem.* 55, 398; *Wien. Akad. Ber.* 8, 31.

E. WILLIGK. *Wien. Akad. Ber.* 8, 22; *Ann. Pharm.* 82, 339; *J. pr. Chem.* 58, 118; *Pharm. Centr.* 1852, 373; *Chem. Gaz.* 1852, 275.

Occurrence. In the root (Rochleder); in the leaves (Willigk) of *Rubia tinctorum*. In the herb of *Asperula odorata, Galium verum,* and *G. Aparine* (Schwarz).

Preparation. This acid occurs in traces in the precipitate *a*, produced by neutral acetate of lead in the plant-organs just mentioned; in somewhat larger quantity in the precipitate *b*, produced in the filtrate by basic acetate of lead; and chiefly in the precipitate *c*, produced by ammonia in the liquid filtered from the preceding precipitates, and still containing lead.

a, *From Madder.* The precipitate *c* is suspended in water, through

which hydrosulphuric acid is passed, and the liquid is filtered, the ruberythric acid then remaining with the sulphide of lead, while acetic acid, sugar, and rubichloric acid pass into the solution. The solution of rubichloric acid obtained in this manner, or in the preparation of ruberythric acid (p. 42), is digested with animal charcoal in a closed vessel at a moderate heat for 24 hours ; and the filtrate is mixed with basic acetate of lead, filtered from the scanty precipitate, and treated with ammoniacal solution of neutral acetate of lead, which throws down the sugar and rubichloric acid. The precipitate is washed with alcohol, suspended in absolute alcohol, and decomposed by hydrosulphuric acid ; the liquid is filtered from the sulphide of lead, which retains the greater part of the sugar ; and the filtrate is evaporated in vacuo, over oil of vitriol and sticks of potash ; a residue is then left which contains rubichloric acid together with a little sugar, and from which the rubichloric acid may be extracted by absolute alcohol (Rochleder.) — b. *From the herb of Asperula odorata.* The precipitate *c* is washed with alcohol, suspended in absolute alcohol, and decomposed by hydrosulphuric acid, and the liquid filtered from the sulphide of lead, and freed from excess of hydrosulphuric acid, is again treated with an alcoholic solution of neutral acetate of lead, and a small quantity of ammonia, whereby rubichlorate of lead is precipitated, to be dried in vacuo over oil of vitriol and sticks of potash. (Schwarz). — c. *From the leaves of Rubia tinctorum.* The precipitate *b* washed with water and suspended in water is decomposed by hydrosulphuric acid ; the liquid is filtered, freed from excess of hydrosulphuric acid, and precipitated with neutral acetate of lead ; the citrate of lead thus precipitated is removed, and the filtrate is mixed with strong alcohol, which throws down an additional quantity of citrate of lead, to be removed by filtration. The alcoholic filtrate mixed with a large quantity of water, and then with basic acetate of lead, deposits rubichlorate of lead, which is to be washed and decomposed with hydrosulphuric acid. The liquid filtered from the sulphide of lead thus produced, and again treated with basic acetate of lead, yields a precipitate, which when washed and dried at $100°$, constitutes rubichlorate of lead *c*. — If the liquid filtered from the precipitate *b* be mixed with a few drops of ammonia, the strongly concentrated filtrate completely precipitated by ammonia, the precipitate digested with warm alcohol, washed therewith, and decomposed under water by hydrosulphuric acid, a filtrate is obtained, containing rubichloric and hydrosulphuric acids. The hydrosulphuric acid is expelled, the liquid mixed with neutral acetate of lead, then with spirit of $40°$, whereby a precipitate is obtained, which, when washed with the same spirit, and dried at $100°$, constitutes rubichlorate of lead *d* (Willigk).

Properties. Colourless or slightly yellow amorphous mass, having a faint, nauseous taste, but destitute of odour.

It appears to be identical with Schunck's *chlorogenin* (Kr.).

Decompositions. 1. The solution of rubichloric acid evaporated over the water-bath acquires a brownish yellow colour, and leaves a sticky mass. — 2. Heated with *hydrochloric acid,* it turns blue, then green, and deposits dark green flocks of chlororubin, with simultaneous production of formic acid (Rochleder, Schwarz).

$$C^{14}H^8O^9 \quad = \quad C^2H^2O^4 \quad + \quad C^{12}H^4O^3 \quad + \quad 2HO$$

Rubichloric acid.   Formic acid.   Chlororubin.
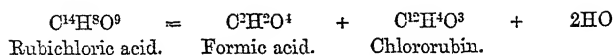
3. By boiling with *nitric acid*, it is converted into oxalic acid (Willigk).

Combinations. Easily soluble in *water.* — *Alkalis* colour it yellow, and acids again destroy the colour. It is not precipitated by baryta-water.

Rubichlorate of lead. (p. 67). — Rubichloric acid forms no precipitate with neutral acetate of lead, and only a slight one with the basic acetate. — The lead-salt is obtained by precipitating rubichloric acid with an ammoniacal solution of neutral acetate of lead, and the bulky white precipitate is dried in vacuo (Rochleder). Yellow transparent mass (Schwarz).

Calculation a, according to Rochleder.   *b, according to* Schwarz.

		Rochleder.					Schwarz.	
84 C	....	13·01	....	13·05	42 C	....	17·50	.... 17·56
59 H	....	1·52	....	1 58	30 H	....	2·08	.... 2·09
65 O	....	13·44	....	13·43	33 O	....	18·34	.... 18·27
25 PbO	....	72·03	...	71·94	8 PbO	....	62·08	.... 62·08

$C^{84}H^{59}O^{65},25PbO$ .... 100·00   .... 100·00 $C^{42}H^{30}O^{33},8PbO$ .... 100·00   .... 100·00

Calculations according to Willigk.

			Willigk. at 100°.				Willigk. at 100°.
		c.				*d.*	
28 C	....	8·60	.... 8·56	140 C	....	16·95	.... 16·85
23 H	.. ..	1·18	.... 1·19	90 H	....	1·82	.... 1·92
25 O	....	10 24	. . 10·21	100 O	... .	16·14	.... 16·30
14 PbO	. ...	79·98	.... 80 04	29 PbO	....	65·09	.... 64·93

$C^{28}H^{23}O^{25},14PbO$ .... 100·00   .... 100·00 $C^{140}H^{90}O^{100},29PbO.$ 100·00   .... 100·00

$a = 11(PbO,HO) + 2(C^{14}H^8O^9,3PbO) + 4(C^{14}H^8O^9,2PbO)$ (Rochleder). — $b = 6(PbO,HO) + 3C^{14}H^8O^9 + 2PbO$ (Schwarz).—$c = C^{14}H^8O^9,3PbO + C^{14}H^8O^9,4PbO + 7(PbO,HO)$.—$d = 10(C^{14}H^8O^9,HO) + 29PbO$ (Willigk).

Rubichloric acid dissolves easily in *alcohol*, but is insoluble in *ether* (Rochleder).

b. Substances agreeing partly with Chlorogenin, partly with Rubian.

1. Higgin's Xanthin.

HIGGIN.   *Phil. Mag. J.* 33, 282 ; *J. pr. Chem.* 46, 1.

Occurrence. In madder-root.

Preparation. (xiv. 135.)

Testing for Xanthin.— A fresh, filtered infusion of madder is precipitated with basic acetate of lead; the precipitate is washed and decomposed by hydrosulphuric acid, and the sulphide of lead is several times boiled out with water. On neutralising the decoctions with

ammonia, and digesting with a small quantity of hydrate of alumina, which throws down rubiacin and alizarin, then evaporating the filtrate, and exhausting the residue, xanthin remains behind (Higgin). — This process yields rubian and its products of decomposition (Schunck).

Dark-brown deliquescent gum, having a bitter taste, but neither sweet nor astringent. When *heated* it melts, blackens, chars, and burns away without residue. — With dilute *sulphuric* or *hydrochloric acid* it assumes a green colour, and when boiled with either of these acids in aqueous solution deposits a green powder (because it contains chlorogenin, Schunck). With *oil of vitriol* it forms a solution of a fine orange colour, changing to carmine-red when heated, from which water throws down yellow flocks soluble with fine crimson colour in ammonia, and probably consisting of Higgin's rubiacin. When boiled for an hour with oil of vitriol, it forms a brown solution, from which water throws down brown flocks, not altered by ammonia. — See also vol. xiv. p. 130, for the decompositions of aqueous extract of madder, which, according to Higgin, result from the presence of xanthin.

Xanthin dissolves readily in *water*, forming a solution of a fine yellow colour. It dissolves with purple-red colour in *alkalis*.

The aqueous solution is precipitated dark-red by *alum* and by *hydrate of alumina*. It is not precipitated by *neutral acetate of lead*, but completely by the *basic acetate*; the precipitate dissolves sparingly in cold, somewhat more readily in hot water, and easily in acetic acid.

It dissolves easily in *alcohol*, sparingly in *ether*. It does not dye mordanted fabrics.

2. Kuhlmann's Xanthin.

Kuhlmann obtains his xanthin (which seems to consist essentially of rubian) from the alcoholic extract of madder-root. He exhausts this extract with cold water, which dissolves fat and alizarin as well as xanthin, precipitates the two former with neutral acetate of lead, filters, and mixes the filtrate with excess of baryta-water, which throws down the lead-compound of xanthin. The precipitate, after washing with dilute baryta-water, is decomposed by dilute sulphuric acid, the liquid then filtered, the yellow filtrate neutralised with baryta-water, and evaporated to dryness. From the residue, alcohol extracts xanthin, leaving sulphate of baryta together with a brown substance. In this manner a brown-yellow extract is obtained, having at first a sweet, then a strong bitter taste; it dissolves readily in water and in alcohol, sparingly in ether. The aqueous solution is coloured lemon-yellow by acids, reddish-yellow by alkalis, and not precipitated by metallic salts; but it forms dark-red or rose-coloured lakes with several metallic oxides, and imparts to mordanted fabrics a brilliant orange-yellow colour (Kuhlmann, *J. Pharm.* 14, 354). By the use of baryta and oxide of lead in this process, decomposition-products are obtained from the rubian of the madder (Schunck).

3. Madder-yellow.

Runge obtains his madder-yellow by precipitating the aqueous infusion of madder (prepared by 12 hours' maceration with 16 pts. water) with lime-water, filtering off the precipitate contain-

ing the madder-yellow and the red colouring matters, which forms
after 12 hours, and decomposing it with acetic acid, the madder-
yellow then passing into solution, still however contaminated with red
colouring matters. The latter are removed by boiling the solution with
wool, mordanted with alum, as long as the wool is coloured red
thereby, then taking it out, and evaporating the liquid. The light yellow
residue is dissolved in alcohol; the madder-yellow is thrown down by
alcoholic neutral acetate of lead, as a scarlet precipitate, which is to
be rinsed with alcohol, dissolved in water, and decomposed by hydro-
sulphuric acid, whereby the madder-yellow is separated from the lead-
oxide.   On evaporating the filtrate, it remains in the form of a yellow
gum. — This gum can scarcely contain rubian, inasmuch as that substance no
longer exists in the madder infusion after the lapse of 12 hours (Kr.).

c. Decomposition-product of Chlorogenin.

Chlororubin.

DEBUS.   *Ann. Pharm.* 66, 355.
SCHUNCK.   See memoirs cited under Rubian (p. 32), 1 and 3.
ROCHLEDER.   See Rubichloric acid (p. 66).
R. SCHWARZ.   *Ibid.*
v. ORTH.   *Wien. Akad. Ber.* 13, 510.

Formation and Preparation. (p. 67). 1. Separates as a dark-green
powder on boiling chlorogenin with acids (Schunck).   When the
aqueous decoction of madder is treated with hydrate of lead to remove
the colouring matters (xiii. 327), the yellow filtrate precipitated with
alcohol, and the plumbiferous precipitate separated by filtration, the
solution retains, together with sugar, a peculiar substance (Schunck's
chlorogenin, Rochleder's *rubichloric acid*), which separates in green flocks
on boiling with acids, the liquid at the same time acquiring a green
colour (Debus). — 2. Rubichloric acid boiled with hydrochloric acid
turns blue, then green, and deposits a dark green powder, also flocks
and films having a red coppery lustre; they may be dried in vacuo
(Rochleder).

From Chinese yellow pods, the fruit of *Gardenia grandiflora* (Jessen,
Wien. Akad. Ber. 14, 294), chlororubin is obtained, according to
v. Orth, by the following process.   The decoction of the yellow pods
prepared with alcohol of 40° is freed from alcohol by distillation in a
stream of carbonic acid; the oil which separates is removed by means
of a wet filter; and the filtrate is treated with neutral acetate of lead,
which throws down colouring matters and tannic acid.   On gently
warming the filtrate with hydrochloric acid, then heating it to the
boiling point, after removing the brown flocks which separate at first,
dark green flocks of chlororubin are deposited, to be washed with
water and dried in vacuo.   They still contain 5·88 p. c. ash (v. Orth).

Properties.   Blue-green, glass-green, or black-green powder, vary-
ing in colour according to the quantity of hydrochloric acid used in its
preparation, the time during which it has been heated and the tem-
perature to which it has been raised.   After drying in vacuo, it
contains variable quantities of water (Rochleder).

Calculations.

Rochleder. a.		Rochleder. b.		Debus.	
60 C	63·94	24 C.......	68·90	30 C....	63·82
27 H.......... .	4·79	9 H	4·31	14 H	4·96
22 O	31·27	7 O.............	26·79	11 O............	31·22
$C^{60}H^{27}O^{22}$	100·00	$C^{24}H^{9}O^{7}$ ....100·00		$C^{30}H^{14}O^{11}$ ....100·00	

Schwarz. c.		v. Orth. d.	
12 C	61·01	48 C	74·81
6 H	5·08	25 H	6·49
5 O................	33·91	9 O	18·70
$C^{12}H^{6}O^{5}$	100·00	$C^{48}H^{25}O^{9}$ ....100·00	

Analyses.

	a. Debus. mean.	b. Rochleder. in vacuo.	c. Schwarz. in vacuo.	d. v. Orth. after deduction of ash.
C	63·81	68·61	61·17	74·82
H	4·98	4·39	5·07	6·46
O	31·21	27·00	33·76	18·72
	100·00	100·00	100·00	100·00

The composition of anhydrous chlororubin agrees, according to Rochleder, with the formula $C^{12}H^{4}O^{3}$; in *a* it is united with ⅞ at., in *b* with ½ at., in *c* with 2 at. water.

Chlororubin exposed to the *air*, acquires a violet colour, taking up ammonia and oxygen. — At 100° it becomes dung-coloured (Rochleder). Decomposed by *nitric acid.*

Insoluble in *water* (Debus). Dissolves in *alkalis*, forming a blood-red solution (Rochleder), which is turned green by acids.

Insoluble in *alcohol* (Debus).

Glucosides with 22 Carbon-atoms in the Copula, and Substances of Cognate Origin.

1. Xanthorhamnin.

$$C^{44}H^{28}O^{28} = C^{22}H^{8}O^{8},2C^{12}H^{10}O^{10}.$$
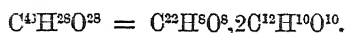
KANE. *Phil. Mag. J.* 23, 3 ; *J. pr. Chem.* 29, 481 ; *N. Ann. Chim. Phys.* 8, 380.

GELLATLY. *N. Edinb. Phil. J.* 7, 252.

ORTLIEB. *Mulhous. Soc. Bull.* 30, 16.

Among the bodies denoted by names derived from *Rhamnus*, *Rh. catharticus* and *Rh. Frangula* (*Handbuch*, viii ; *Phytochem.* 23), we have to distinguish : a. *Substances from Persian* or *Turkey berries* (*Graines d'Avignon*, *Graines de Perse*, *Gelbbeeren*). According to Kane, *Chryso-*

rhamnin and *Xanthorhamnin;* according to Gellatly, *Xanthorhamnin* (with the decomposition-product *Rhamnetin*); according to Ortlieb, *Hydrate of oxyrhamnin, Rhamnin* and *Hydrate of rhamnin;* according to Preisser, *Rhamnin* and *Rhamnein.* — b. *Substances from the bark of Rhamnus Frangula* and *Rh. catharticus;* Buchner and Binswanger's *Rhamnoxanthin,* identical with Casselmann's *Frangulin.* — c. *Substances from the berries of Rhamnus catharticus.* Fleury, Winckler and Binswanger's *Rhamnin;* also an uncrystallisable bitter substance called *cathartin* by Hubert, *Rhamnocathartin* by Binswanger.

Some of these bodies are perhaps identical with others from the same sources, or from different sources. Gerhardt (*Traité,* 4, 281) regards Fleury's rhamnin and Kane's chrysorhamnin as identical (incorrectly [Kr.]). Hlasiwetz (*Wien. Akad. Ber.* 17, 381) formerly regarded rhamnoxanthin as identical with quercitrin and with euxanthic acid. — Ortlieb suggests the identity of his hydrate of oxyrhamnin with euxanthic acid. — More recently, Hlasiwetz regards xanthorhamnin and rhamnetin as identical with quercitrin and quercetin ; this is doubted by Bolley (who, however, found quercetin in Persian berries : *Chem. Soc. Qu. J.* 13, 328), also by Gellatly (*Chem. News* 3, 196; *Kopp's Jahresber.* 1860, 497). The statement of Hubert that this rhamnocathartin is identical with the sennescathartin of Lassaigne & Feneulle, has been shown to be incorrect by Winckler.

Chevreul (*Leçons sur la teinture*) obtained from Persian berries a yellow volatile substance, and a red colouring matter.   Respecting Preisser's *Rhamnin* and *Rhamnein,* see *Rev. scient.* 16, 61; *J. pr. Chem.* 32, 159 ; also xv, p. 28 of this work. — For greater clearness, the results obtained by Kane, Gellatly and Ortlieb, which do not agree well together, will be separately described.

a. According to Kane. — Xanthorhamnin occurs only in ripe Persian berries, being formed from the chrysorhamnin (p. 75) of the unripe berries. When the unripe berries are boiled with water for some minutes and then dried, chrysorhamnin can no longer be found in them, but only xanthorhamnin. Xanthorhamnin is likewise produced by boiling chrysorhamnin with water in contact with the air. — Xanthorhamnin dried in vacuo over oil of vitriol is deliquescent, but melts below 100°, and continues to give off water till heated to 200°, and then solidifies to a brittle mass. It decomposes above 200°, dissolves readily in water and alcohol, but is quite insoluble in ether.

	In vacuo.			Kane.
23 C	138	34·78		34·74
27 H	27	6·80		6·93
29 O	232	58·42		58·33
$C^{23}H^{14}O^{14}$ + 15HO	397	100·00		100·00

	at 100°.			Kane.	
23 C	138	50·92	49·97	51·20
13 H	13	4·80	5·18	5·28
15 O	120	44·28	41·85	43·52
$C^{23}H^{12}O^{14}$ + HO	271	100·00	100·00	100·00

	at 150°.			Kane.
23 C	138	52·67	52·55
12 H	12	4·58	5·15
14 O	112	42·75	42·30
$C^{23}H^{12}O^{14}$	262	100·00	100·00

Lead-compound of Xanthorhamnin. Obtained by precipitating : *a.* neutral acetate, and *b.* basic acetate of lead with xanthorhamnin. The compounds thus precipitated are not pure, each being contaminated with the other.

		a.	at 100°.				Kane.
23	C	....	138·0	....	26·93	....	26·58
15	H	....	15·0	....	2·93	. ...	2·86
17	O	. ...	136·0	....	26·54	....	25·20
2	PbO	....	223·4	....	43·60	....	45·36

$C^{23}H^{12}O^{14},2PbO + 3aq$......... 512·4 .... 100·00 .... 100·67

		b.	at 100°.				Kane. mean.
23	C	....	138·0	....	21·20	....	21·89
18	H	....	18·0	....	2·76	....	2·94
20	O	....	160·0	....	21·57	....	23·74
3	PbO	... .	335·1	....	51·47	....	51·34

$C^{23}H^{12}O^{14},3PbO + 6aq$ .... 651.1 .... 100·00 .... 100·00

So, according to Kane.

b. According to Gellatly. — The coarsely ground unripe berries are boiled with alcohol; and the tincture, not too concentrated, is freed by standing and repeated decantation, from a dark brown resin which gradually separates, and then left for some days to crystallise, the liquid ultimately solidifying to a crystalline magma. The product is purified by repeated crystallisation from alcohol. By agitating the tincture, crystals may be more quickly obtained, but they are then less pure.

The hydrated crystals of xanthorhamnin give off their water at the heat of the water-bath, and do not melt even at 130°. Nearly tasteless.

		Dehydrated.				Gellatly. mean.
46	C	....	276	....	52·27	....	52·10
28	H	.. ..	28	....	5·30	....	5·78
28	O	....	224	....	42·43	....	42·12

$C^{46}H^{28}O^{28}$ .... 528 .... 100·00 .... 100·00

Aqueous xanthorhamnin is resinised by *bromine* and *chlorine.* — It is oxidised by boiling with *nitric acid,* forming a red solution, which contains oxalic acid. It dissolves in *oil of vitriol* and is thrown down as a yellow precipitate by water. Dilute *acids* decompose xanthorhamnin at the boiling heat, into rhamnetin and glucose :

$$C^{46}H^{28}O^{28} + 6HO = C^{22}H^{10}O^{10} + C^{24}H^{24}O^{24}.$$
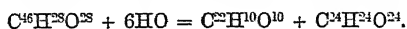
From an alcoholic solution of xanthorhamnin, *caustic potash* throws down a hard reddish resin. — By boiling with *baryta-water*, a red substance is formed, which instantly turns black in contact with the air.

Combinations. *With Water.* — Crystallised xanthorhamnin forms compact tufts of pale yellow, silky shining crystals, which, at the

heat of the water-bath, give off, on the average, 14·37 p. c. water. (10 at. HO = 14·56 per cent.)

It dissolves easily in water both hot and cold, but cannot be separated from the solution in the crystalline form.

With aqueous *alkalis*, it forms brown solutions, which become paler when mixed with acids. — It precipitates the solutions of *alkaline earths*, *alumina* and *stannic salts*. The yellow precipitates are not easily obtained of definite composition.

With Lead-oxide. — Precipitated by neutral acetate of lead from excess of alcoholic xanthorhamnin. The air-dried yellow precipitate gives off 8·66 p. c. water when dried. (8 at. HO = 8·74 per cent.)

		at 100°.			Gellatly.
46	C	276·0	....	36·70	37·70
28	H	28·0	....	3·73	4·08
28	O	224·0	....	29·82	31·43
2	PbO	223·6	....	29·75	26·79
$C^{46}H^{28}O^{28},2PbO$		751·6	....	100·00	100·00

Xanthorhamnin forms a black precipitate with *iron-solutions*. It dissolves in cold, very easily in boiling *alcohol*, not in *ether*. From the hot, highly concentrated alcoholic solution, it separates as a semi-fluid resin which becomes crystalline when covered with alcohol. It dyes fabrics mordanted with alumina of a fine yellow, those mordanted with iron, black.

c. According to Ortlieb, Persian berries contain a glucoside, which yields the following substances as products of decomposition. The fresh decoction of the berries does not contain any sugar, but after the colouring matter has been deposited, the supernatant liquid contains a large quantity of sugar. When fermented, it deposits: first — golden-yellow crystalline grains (*a*), then yellow-green flocks (*b*), both of which are obtained in variable quantities from different sorts of Persian berries. If the mother-liquors are boiled with dilute sulphuric acid, additional flocks (*c*) are deposited. Of these, *a* is Ortlieb's *Hydrate of Oxyrhamnin* existing ready formed in the berries, isomeric, and perhaps identical, with euxanthic acid. — *b.* Ortlieb's *Hydrate of Rhamnin*, insoluble in water, soluble in boiling alcohol, and crystallising therefrom on cooling. — *c.* Ortlieb's *Rhamnin*, more soluble in water than *a* or *b*, and crystallisable from alcohol. — All these substances form conjugated acids with sulphuric acid.

	a.			Ortlieb.
42 C	55·50	...	....	55·4
18 H	4·12	.	....	4·3
22 O	40·38		....	40·3
$C^{42}H^{18}O^{22}$	100·00		....	100·0

	b.		Ortlieb.		*c.*		Ortlieb.
42 C	58·60	....	58·9	42 C	60·11	....	60·7
18 H	6·18	....	6·5	16 H	3·88	....	3·7
20 O	35·22	....	34·6	18 O	36·01	....	35·6
$C^{42}H^{18}O^{20}$	100·00	....	100·0	$C^{42}H^{16}O^{18}$	100·00	....	100·0

All dried at 140°.

Appendix to vol. xv, p. 530.

1. Rhamnetin.

$$C^{22}H^{10}O^{10} = C^{22}H^{10}O^8,O^2?$$
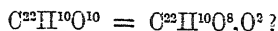
GELLATLY. *N. Edinb. Phil. J.* 7, 256.

Formation and Preparation. — 1. When xanthorhamnin is boiled with dilute sulphuric or hydrochloric acid, rhamnetin falls to the bottom, while glucose remains in solution (p. 73). — 2. When the berries of *Rhamnus tinctoria* are stirred up with cold water, the xanthorhamnin contained in them is converted, by influences not well understood, into rhamnetin, which is deposited from the filtrate in the form of a yellow powder.

Soft, pale yellow, nearly tasteless crystals.

					Gellatly.
					mean.
22 C	132		59·46		59·37
10 H	10		4·50		4·41
10 O	80		36·04		36·22
$C^{22}H^{10}O^{10}$	222		100·00		100·00

Nearly insoluble in *water*, easily soluble in *alkalis*, and precipitated therefrom by acids. — Insoluble in *alcohol* and *ether*.

2. Chrysorhamnin.

$$C^{46}H^{22}O^{22}.$$
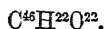
KANE. *Phil. Mag. J.* 23, 3; *J. pr. Chem.* 29, 481; *Dingl.* 5, 89; *N. Ann. Chim. Phys.* 8, 380.

Occurs in the unripe berries of *Rhamnus tinctoria*, known in commerce as Persian berries (their inner surface is covered with a yellow coating), but disappears as the fruit ripens, passing into xanthorhamnin. Gellatly did not obtain it from these berries, either ripe or unripe. (See the remarks on substances obtained from various species of Rhamnus (pp. 7, 72).

It is extracted from the berries by ether. — Stellate needles, having a fine golden-yellow colour and silky lustre.

	at 100°.				Kane.		
46 C	276		58·23		58·23		57·81
22 H	22		4·64		4·77		4·64
22 O	176		37·13		37·00		37·55
$C^{46}H^{22}O^{22}$	474		100·00		100·00		100·00

When chrysorhamnin is boiled with *water*, the dissolved portion separates as xanthoramnin. — It is not altered by *acids*, but *alkalis* dissolve it, and apparently decompose it at the same time.

It is nearly insoluble in cold water.

Lead-compound. — Alcoholic chrysorhamnin throws down from neutral acetate of lead, a precipitate of a fine yellow colour, containing 48·62 p. c. lead. — With basic acetate of lead, a yellow precipitate is obtained containing 6 at. PbO to 1 at. chrysorhamnin.

		at 100°.			Kane.
46	C	276 0	.... .	29·98	.... 29 62
22	H	22·0	.....	2·39	.. . 2 19
22	O	176·0	....	19·11	.... 19·59
4	PbO	446 8	..	48·52	.... 48 60

$$C^{46}H^{22}O^{22},4PbO .... 920·3 .... 100·00 .... 100 00$$

Chrysorhamnin is soluble in *alcohol*, but is not recovered from the solution by evaporation, inasmuch as it decomposes. — It dissolves in *ether*, and crystallises undecomposed when the solution is left to evaporate.

3. Frangulin.

$$C^{12}H^6O^6 \text{ or } C^{40}H^{20}O^{20}.$$
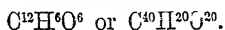
BINSWANGER.   *Repert.* 104, 151.

WINCKLER.   *Repert.* 104, 145.

L. A. BUCHNER, JUN.   *Ann. Pharm.* 87, 218; *J. pr. Chem.* 59, 343; *N. J. Pharm.* 33, 79.

PHIPSON.   *Compt. rend.* 47, 153; *N. Repert.* 8, 69.—*Chem. News,* 1861, 255; *Rép. Chim. pure,* 3, 216. ·

CASSELMANN.   *Ann. Pharm.* 104, 77; *Kopp's Jahresber.* 1857, p. 522.

Rhamnoxanthin of Buchner and Binswanger.   Appears to have been discovered by Buchner, but was first mentioned by Binswanger, and was first prepared pure and examined by Casselmann. — An acrid extractive bitter principle and a yellow resinous colouring matter from the bark of *Rhamnus Frangula,* were described by Gerber (*Br. Arch.* 26, 8); the latter behaves to alkalis and acids in the same manner as frangulin.   Winckler further distinguishes a red colouring matter, from the bark, lying below the epidermis in the layer of bast: it is precipitated from the concentrated alcoholic tincture by ether.   Binswanger (*Repert.* 104, 181) distinguishes from frangulin, a bitter substance from the stem- and root-bark of *Rhamnus catharticus,* which crystallises in white needles, is prepared as described at page 2 (with basic acetate of lead), and dissolves easily in water, sparingly in strong alcohol and in ether. — See the observations on substances obtained from Rhamnus at pages 71, 72.

Occurrence.   In the root- and stem-bark of *Rhamnus catharticus* and *Rh. Frangula* (Buchner, Binswanger).   On the inner surface of a piece of root-bark of *Rh. Frangula,* which had been kept for a long time, Buchner observed golden-yellow needles of frangulin to separate.   In the bast and the vessels of the medullary sheath of the branches of *Rh. Frangula* (Phipson).   It appears to be partly formed from an amorphous resinous body, when the bark is left to itself, inasmuch as old bark yields a larger quantity of frangulin than that which has been recently collected (Casselmann). — It is found in the seeds of both species of Rhamnus (Buchner).

Preparation. 1. The branches of the berry-bearing alder (*Rh. Frangula*) are macerated for three or four days in bisulphide of carbon; the extract is evaporated to dryness; and the residue is exhausted with alcohol, which leaves fat undissolved, again evaporated, and recrystallised from ether (Phipson). — 2. The comminuted bark of the stem or branches is exhausted with ammoniacal water; the extracts are supersaturated with hydrochloric acid, and left to themselves for several weeks, or as long as the resulting black-brown precipitates continue to increase. These precipitates are collected, washed, and boiled with alcohol of 80 per cent. with addition of neutral acetate of lead. The hot filtrate mixed with water till it becomes turbid, then well boiled, and set aside for several days, deposits frangulin, which may be recrystallised from boiling alcohol (Casselmann). The solution prepared as above with addition of neutral acetate of lead, and filtered from the lead-precipitate, may also be shaken up with hydrated oxide (or basic acetate) of lead, which precipitates all the frangulin. On immersing the precipitate in water containing alcohol, decomposing it with hydrosulphuric acid, and then boiling with alcohol, the alcohol takes up the frangulin, which may be crystallised from the solution mixed with water, and recrystallised from alcohol. Frangulin thus prepared is apt to be mixed with sulphur derived from the sulphuretted hydrogen (Casselmann). Winckler dissolves the precipitate thrown down by hydrochloric acid in alcohol, evaporates, and exhausts the residue with ether.

Properties, — Lemon-yellow crystalline masses having a dull silky lustre, and appearing under the microscope to be formed of opaque quadratic tables. Melts at 249° (250° Phipson), with evolution of yellow vapours, and sublimes, with partial decomposition, in golden-yellow needles (Casselmann). Volatilises slowly, even at mean temperatures (Buchner, Binswanger). Tasteless and inodorous.

		at 100°.		Casselmann. *mean.*
12 C	72	57·14		57·19
6 H	6	4·76		4·98
6 O	48	38·10		37·83
$C^{12}H^6O^6$	126	100·00		100·00

According to Hesse (*Ann. Pharm.* 117, 349) the formula is $C^{40}H^{20}O^{20}$, which requires the same percentage composition and agrees better with that of nitro-frangulic acid. Casselmann compared frangulin with chrysophanic acid, without however finding them to be identical. Hlasiwetz (*Wien. Akad. Ber.* 17, 381) regards frangulin as similar to euxanthic acid and quercitrin, but this resemblance also is not borne out by Casselmann's investigation.

Decompositions. 1. Fuming *nitric acid* converts frangulin into nitro-frangulic and oxalic acids (Casselmann). — 2. *Reducing agents* colour it brown (Phipson). — 3. Cold *oil of vitriol* dissolves it with dark ruby-red colour, changing to brown on heating; the solution is precipitated by water. (Casselman). Frangulin immersed in oil of vitriol immediately acquires a fine emerald-green colour, changing in a few seconds to purple, then to red, and on addition of water, to yellow. If the oil of vitriol be poured off as soon as the frangulin has turned green, the green colour remains constant, and is not altered, either by alkalis or by dilute acids (Phipson).

Frangulin is insoluble in *water*. — It is insoluble in cold *nitric acid ;* but dissolves completely in the hot acid, and crystallises unchanged on cooling (Casselmann).

It dissolves slowly in cold, more quickly in warmed aqueous *ammonia* and in aqueous *fixed alkalis*, with splendid purple colour (Casselmann). The resulting compounds are soluble in water, alcohol and ether, but not in bisulphide of carbon (Phipson). It is precipitated from the alkaline solutions by acids. It is not precipitated by *metallic salts*, but forms finely coloured lakes with *hydrated metallic oxides* (Casselmann). The ammoniacal solution supersaturated with citric acid forms a beautiful violet lake with magnesia (Phipson).

Frangulin dissolves in 160 pts. of warm alcohol of 80 per cent., and separates out almost completely on cooling. Nearly insoluble in *ether* (Casselman). Impure frangulin dissolves readily in ether and in alcohol (Phipson). — Frangulin dissolves in *bisulphide of carbon* (Phipson), in *oil of turpentine*, and in *fixed oils* (Casselmann). Frangulin dyes silk, wool and cotton (Phipson).

4. Nitrofrangulic Acid.
$$C^{40}X^5H^{11}O^{16} ?$$
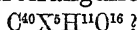
Casselmann (1857).   *Ann. Pharm.* 104, 84.

Formation. By heating frangulin with fuming nitric acid, oxalic acid being formed at the same time (Casselman, see below).

$$4C^{12}H^6O^6 + 14NO^4 = C^{40}H^{11}X^5O^{17} + 2C^4H^2O^8 + 9HO + 9NO^2$$
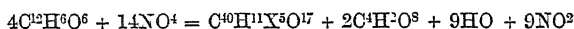
Preparation. Frangulin is dissolved in warm fuming nitric acid; the solution after dilution with water is carefully evaporated nearly to dryness over the water-bath, and the residue is washed with water, till the water which runs off begins to assume a dark red colour. The residue is crystallised either from acidulated water or alcohol, in which case, however, the crystallisation is not complete for several months; — or more quickly the acid is converted into a silver-salt; this salt is dissolved in boiling alcohol or water and decomposed by hydrochloric acid; and the precipitated chloride of silver is separated, whereupon the filtrate soon deposits crystals.

Properties. Separates from water in small yellow tables, from alcohol in stellate groups of long silky-shining orange-coloured needles. Tastes harsh and rather bitter ; colours the saliva purple-red.

at 100°.

40	C	240	38·89
5	N	70	11·34
11	H	11	1·78
37	O	296	47·99
$C^{40}X^5H^{11}O^{17}$		617	100·00

				Casselmann. mean.	Phipson.
40	C	240	39·41	38·7	39·0
5	N	70	11·50	11·4	11·4
11	H	11	1·80	2·0	1·9
36	O	288	47·29	47·9	47·7
$C^{40}X^5H^{11}O^{16}$		609	100·00	100·0	100·0

Casselman gives the first formula; O. Hesse (*Ann. Pharm.* 117, 349) the second. The formula $C^{12}N^2H^4O^{12}$ proposed by Phipson (*Rép. Chim. pure*, 3, 317), is improbable in itself and does not agree with the analyses. A. Wurtz (*Rép. Chim. pure*, 3, 317) regards nitrofrangulic acid as a mixture of nitro- and binitro-frangulin, a supposition which does not accord with Casselmann's analyses of the salts. Weltzien's formula $C^{40}X^5H^9O^{36}$,HO (*Verbind.* 645) supposes the salts to contain 1 at. water of crystallisation (Kr.).

Decompositions. 1. The acid detonates and leaves charcoal when *heated*. 2. The hot aqueous solution, when *hydrosulphuric acid* is continuously passed into it, assumes a violet-blue colour, with separation of sulphur, and afterwards yields a violet-blue precipitate with hydrochloric acid.

Combinations. The acid dissolves sparingly in cold *water*, with dark carmine-red colour in hot water, and separates slowly on cooling, more quickly on addition of acids, in crystalline flocks. — It is coloured light yellow by cold *oil of vitriol*, red-brown by hot. — It dissolves in strong *nitric acid*, and crystallises therefrom.

Nitrofrangulic acid unites with *bases.* It dissolves with violet-red colour in aqueous *alkalis*, and its aqueous solution forms fiery-red precipitates with baryta-, strontia-, lime-, cadmium- and lead-salts.

Nitrofrangulate of Copper. — Obtained by adding alcoholic nitrofrangulic acid to aqueous cupric acetate. By the contrary mode of procedure, red flocks are obtained. Violet-blue, non-crystalline flocks, becoming dark violet-red when dry. Detonates violently when heated. Nearly insoluble in water, sparingly soluble in alcohol and ether, easily and with light blue colour in ether.

		at 100°.		Casselmann.	
40	C	240·0	37·1	37·1
10	H	10·0	1·5	1·8
5	N	70·0	10·8	
36	O	288·0	44·5	
	CuO	39·7	6·1	6·6
$C^{40}H^{10}X^5CuO^{17}$		647·7	100·0	

Hesse's formula $C^{4}X^3C^4{}_{d}H^{10}O^{16}$ requires 37·50 p. c. C., 1·56 H., and 6·25 CuO.

Nitrofrangulate of Silver. — Obtained by precipitating an alcoholic or hot aqueous solution of nitrofrangulic acid with aqueous nitrate of silver. — Cinnabar red needles having a dull silky lustre, detonating when heated, sparingly soluble in cold, easily in boiling water, dissolving with dark ruby-red colour in alcohol and ether.

		at 100°.		Casselmann. mean.	
40	C	240	33·1	33·0
10	H	10	1·4	1·5
5	N	70	9·7	
36	O	288	39·8	
	AgO	116	16·0	16·0
$C^{40}H^{10}X^5AgO^{17}$		724	100·0	

Hesse's formula $C^{40}X^5AgO^{16}$, requires 33·52 p.c. C., 1·39 H., and 16·21 AgO.

Nitrofrangulic acid dissolves easily in *alcohol* and *ether*, with dark red colour, and remains behind with yellow colour when the liquid is evaporated.

5. Rhamnin.

FLEURY (1841). *J. Pharm.* 27, 226; *N. B. Arch.* 28, 292; *Repert.* 75, 209.
WINCKLER. *Jahrb. pr. Pharm.* 24, 1.
BINSWANGER. *Repert.* 104, 54.

Exists together with rhamnocathartin in the unripe berries of *Rhamnus catharticus* (pp. 72, 81).

Preparation. The unripe berries are pressed, the juice is removed, the residue is repeatedly boiled with water, and the decoctions are set aside to crystallise. The resulting cauliflower-like crystals are purified by pressure, solution in boiling alcohol, washing the crystals which separate out again with cold water and weak spirit, — then by re-crystallisation from boiling alcohol, with help of animal charcoal (Fleury).

Binswanger macerates the dried berries in cold water, then crushes and presses them. When the juice evaporated to an extract is exhausted with alcohol, the alcoholic extract treated with water, the portion containing the tannin, which remains undissolved, again dissolved in warm alcohol, and this solution left to evaporate, crystals of rhamnin separate out. — The expressed juice, when left to stand, also deposits crystals of rhamnin. It collects on the surface of the juice during fermentation, but is less pure than that obtained from the expressed residue (Fleury).

Properties. — Small pale yellow granules arranged in cauliflower-like groups; rarely needles united in tufts (Fleury). Pale yellow nodules and small silky-shining crystals (Binswanger). Not volatile. — Tasteless (Binswanger), has a faint peculiar taste (Fleury).

Decompositions. When *heated*, it melts, decomposes, and leaves combustible charcoal (Binswanger). — It dissolves, with dark brown colour in hot *nitric acid*; if the heat be continued the solution quickly assumes a pale yellow colour, and leaves on evaporation, a crystalline mass soluble, for the most part, in water, and a bitter yellow powder, probably picric acid. Water added to the highly concentrated nitric acid solution throws down (while oxalic acid remains dissolved) short yellow needles united in fern-like groups, sparingly soluble in cold, more soluble in hot water, and not precipitated by metallic salts. The needles are decolorised by acids, but are obtained otherwise unaltered on evaporating the acid solution. They dissolve in alcohol and in ammonia, with saffron-yellow colour, and crystallise from the latter solution, an amorphous mass likewise remaining (Fleury). Rhamnin is not fermentable (Fleury).

Rhamnin is nearly or quite insoluble in cold *water*, in boiling water it swells up and takes up a large quantity of water. — It dissolves in cold *oil of vitriol* and in cold concentrated *hydrochloric acid*, with saffron-yellow colour, and is precipitated by water. Dissolves in hot dilute sulphuric acid and crystallises on cooling. — Dissolves in aqueous *ammonia* and *potash* with saffron-yellow colour, not purple-red (Binswanger), also in alkaline carbonates, and is precipitated by acids.

The sweet alkaline solutions leave, when evaporated, brown shining masses which become slightly moist on exposure to the air, and colour water strongly (Fleury).

Rhamnin dissolves sparingly in cold, easily in boiling *alcohol*, but is insoluble in ether.

6. Rhamnocathartin.

HUBERT. *J. Chim. méd.* 6, 193 ; *Br. Arch.* 34, 142 ; *Repert.* 35, 293.
F. L. WINCKLER *Jahrb. pr. Pharm.* 19, 221 ; 24, 1.
BINSWANGER. *Repert.* 104, 54.

The uncrystallisable bitter principle of the berries of *Rhamnus catharticus* (comp. p. 80).

Preparation. 1. The berries are crushed, strained, and pressed, the juice is evaporated to an extract; this extract is exhausted with alcohol of 80 per cent.; the tinctures are treated with animal charcoal; and the alcohol is distilled off. On exhausting the residue with cold alcohol of 98 per cent., treating the strongly bitter brownish tincture with animal charcoal, and evaporating, coloured rhamnocathartin remains ; it must be dissolved in 3 pts. alcohol of 80 per cent., and the solution mixed with 8 or 10 times its volume of ether. After the substances thereby precipitated have completely settled down, the clear ether-alcoholic solution is decanted, decolorised with animal charcoal, and evaporated (Winckler). — 2. The juice of the ripe berries is evaporated to an extract ; this extract is exhausted with hot alcohol, the tincture evaporated, and the residue mixed with water, which separates yellow-green pulverulent rhamno-tannic acid. The filtrate shaken up with coarsely pounded, purified bone-charcoal, as long as it retains any bitter taste, yields rhamnocathartin to the charcoal ; and on washing this charcoal with cold water, drying, treating it with hot alcohol, and evaporating the tincture, the rhamnocathartin is left behind (Binswanger).

Properties. Translucent amorphous, yellowish, brittle mass which may be rubbed to a yellow powder. Emits a peculiar smell when rubbed. Tastes bitter and very repulsive (Winckler), and irritating (Binswanger). Neutral. Tolerably permanent in the air.

When *heated*, it melts to a yellow oil, turns brown, gives off inflammable vapours, and leaves combustible charcoal (Winckler). With *nitric acid*, it yields a large quantity of picric acid (Winckler). — It is not decomposed during the fermentation of the juice (Hubert).

Soluble in all proportions in *water* (Winckler). Insoluble in cold, somewhat soluble in boiling water, to which it imparts a very bitter taste, while the remainder melts and adheres to the sides of the vessel. The hot solution becomes turbid on cooling (Binswanger). The aqueous solution is coloured brownish gold-yellow, without precipitation, by *ammonia*, the *fixed alkalis*, and *basic acetate of lead*, and becomes colourless again on addition of acids. It colours *sesquichloride of iron* dark brown-green (Winckler).

Rhamnocathartin dissolves in all proportions in *alcohol*, but is in

soluble in *ether* (Binswanger, Winckler). It dissolves in *ether-alcohol* (Winckler).

Glucosides with 24 at. Carbon in the Copula.

Globularin.

G. F. WALZ. *N. Jahrb. Pharm.* 7, 1 ; further 13, 281.

The bitter principle of the leaves of the *Globularia Alypum*, known in commerce by the name of false senna leaves.

Preparation. The leaves are exhausted by digestion in alcohol of sp. gr. 0·85 ; the alcohol is distilled from the tinctures ; the residue suspended in water is digested for some time and nearly at the boiling heat, with levigated litharge; the liquid filtered; and the filtrate slowly evaporated over the water-bath. The residue is treated with ether to remove yellow colouring matter, then dissolved in water, and mixed with tannic acid, which precipitates the greater part of the globularin in white flocks, which cake together to a resin, whilst another portion remains dissolved and may be precipitated, though not completely, by saturation with ammonia. The precipitate formed by tannic acid is dissolved in alcohol; the solution mixed with levigated litharge, and heated nearly to the boiling point for several days, with frequent agitation ; and the filtrate, after complete precipitation of the tannic acid, is evaporated to dryness, globularin then remaining. Part of the globularin is precipitated during the digestion of the aqueous solution of the alcoholic extract with litharge, and may be dissolved out from the precipitate by alcohol. It is obtained in the solid state by evaporating the alcohol, and freed from globularesin by washing with ether. — The leaves after exhaustion with alcohol, still contain globularin, which may be obtained by boiling them with water, precipitating the decoction with neutral and basic acetate of lead successively, freeing the filtrate from lead, neutralising with carbonate of soda, and precipitating with tannic acid. From this precipitate globularin is obtained as above.

Properties. White powder having a bitter taste.

					Walz. mean.
60 C	360	....	57·32	....	56·88
44 H	44	....	7·01	....	6 63
28 O	224	....	35·67	....	36·49
C⁶⁰H⁴⁴O²⁸	628	....	100·00	....	100·00

Walz calculates the mean of his analyses incorrectly.

Decompositions. 1. *Burns* without residue on platinum-foil. — 2. Its aqueous solution mixed with *sulphuric acid*, becomes turbid, deposits white resinous globules, and is completely resolved by boiling into globularetin (xv, 38) and paraglobularetin, which separate, and sugar, 28·6 pts. sugar being obtained to 100 pts. globularetin (supposing that

this sugar reduces the same quantity of cupric oxide from an alkaline solution as cane-sugar [or glucose? Kr.]) According to Walz, the reaction is :

$$C^{60}H^{44}O^{23} = C^{24}H^{14}O^{6} + C^{24}H^{16}O^{8} + C^{12}H^{12}O^{12} + 2HO.$$
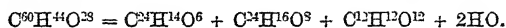
An alcoholic solution of globularin, not quite pure, acquired, by keeping for some months, an agreeable odour of pine-apples, and yielded, by boiling with water, a milky distillate from which ether extracted a fragrant oil. This globularin yielded by boiling with acids the same products as the pure substance, together with a fragrant resin.

Appendix to Globularin.

1. Globularesin.

$C^{40}H^{36}O^{16}$?
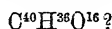
G. F. WALZ. *N. Jahrb. Pharm.* 13, 281.

The fragrant resin of *Globularia Alypum.*
From the alcoholic extract of the leaves, water extracts globularin, while globularesin remains. The residue is dissolved in alcohol, and the filtrate precipitated with water. — Extracted from globularin by ether, in the process of preparing that substance (p. 82).
Olive-green, transparent, kneadable mass, having the odour of globularia leaves.

								Walz.
40	C	....	240	......	59·40	....	59 95
36	H	....	36	....	8·91	....	9·03
16	O	....	128	....	31·69	....	31·02
	$C^{40}H^{36}O^{16}$	....	404	....	100·00	....	100 00

Walz, by an incorrect calculation, arrives at the formula $C^{49}H^{32}O^{10}$ (Kr).

2. Globularitannic Acid.

G. F. WALZ. *N. Jahrb. Pharm.* 13, 287.

The yellow colouring matter of the leaves of *Globularia Alypum,* known only in alcoholic solution and as a lead-salt.
Precipitated from the aqueous solution of the alcoholic extract by digestion with litharge in the manner already described (p. 82).
The precipitate is triturated with alcohol, and decomposed by dilute sulphuric acid ; and the greenish brown filtrate, after being shaken up with a small quantity of carbonate of lead, is precipitated with an alcoholic solution of neutral acetate of lead. This process yields globularitannate of lead.
An alcoholic solution of globularitannic acid, neutralised with ammonia, colours ferric hydrochlorate dark-green, and forms dirty green precipitates with sulphate of copper, mercurous nitrate and oxide of silver.

			Lead-salt at 100°.				Walz.
16	C	....	96	....	21·62	....	21·62
12	H	....	12	....	2·70	....	2·51
14	O	....	112	....	25·23	....	25·6?
	2PbO	....	224	....	50·45	....	50·25
$C^{16}H^{12}O^{14},2PbO$		....	444	....	100·00	....	10·000

With *oil of vitriol*, it forms a brown solution, from which water throws down brown flocks. — It is not altered by *hydrochloric acid;* but *nitric acid* of sp. gr. 1·48 dissolves it with evolution of red vapours. — It dissolves in *ammonia* and in *potash*, and is precipitated by acids.

Saponin.

GEHLEN. *Berl. Jahrb.* 1804, 112.
SCHRADER. *A. Gehl.* 8. 548.
BUCHHOLZ. *Taschenb.* 1811, 38.
PFAFF. *System der Materia medica*, 2, 110.
BLEY. *N. Tr.* 24, 1, 102 ; *Ann Pharm.* 4, 283. — *J. pr. Chem.* 1, 156. — *N. Br. Arch.* 37, 82.
TROMMSDORFF. *N. Tr.* 24, 2, 28.
DULONG. *J. Pharm.* 13, 567.
HENRY & BOUTRON-CHARLARD. *J. Pharm.* 14, 249.
BUSSY. *Ann. Chim. Phys.* 51, 390 ; *J. Pharm.* 19, 1 ; *Ann. Pharm.* 7, 168 ; *Schw.* 68, 81.
FREMY. *Ann. Chim. Phys.* 58, 101 ; *Ann. Pharm.* 15, 187 ; *J. pr. Chem.* 3, 393.
QUEVENNE. *J. Pharm.* 22, 460 ; abstr. *Ann Pharm.* 20, 34, — *J. Pharm.* 23, 270.
MALAPERT. *N. J. Pharm.* 10, 339.
LE BEUF. *Compt. rend.* 31, 652 ; *J. pr. Chem.* 51, 471.
SCHARLING. *Ann Pharm.* 74, 351.
ROCHLEDER & SCHWARZ. *Wien. Akad. Ber.* 11, 335 ; *J. pr. Chem.* 60, 291 ; abstr. *Ann. Pharm.* 88, 356 ; *Lieb. Kopp. Jahresb.* 1853, 554.
BOLLEY. *Ann. Pharm.* 90, 212 ; abstr. *J. pr. Chem.* 63, 92. — *Ann. Pharm.* 91. 117 ; abstr. *J. pr. Chem.* 63, 253.
A. OVERBECK. *N. Br. Arch.* 77, 134.
TH. CRAWFURD. *Pharm. Vierteljahrsschrift*, 6, 361.
TR. ROCHLEDER & V. PAYR. *Wien. Akad. Ber.* 45, 7 ; *Chem. Centr.* 1862, 177.

Sources and History. Occurs in plants of various natural families, especially in the *Silene* (*Handbuch*, viii. *Phytochem.* 33). — In the root and herb of *Saponaria officialis.* Designated by Schrader as *Saponin*, by Dulk as *irritating extractive matter* (*kratzender Extractivstoff*). Respecting Osborne's principle of Saponaria, see p. 91. — In the root of *Gypsophila Struthium*, as formerly suspected by Wahlenberg; the substance thence obtained was called *Struthiin* by Bley, but recognised by Bussy as saponin. — In *Agrostemma Githago* (Malapert), constituting Scharling's *Githagin.* The root, cotyledons and ovaries of this plant contain

saponin, the quantity increasing till the seed ripens; the stalks, leaves, and calices do not contain saponin (Malapert). The seeds contain 0·9 p.c. saponin, but the basic substance *agrostemmine*, existing, according to Schulze (*N. Br. Arch.* 55, 298, and 56, 163) in the seed-shells, is not to be found there (Crawfurd). — In the bark of *Quillaia Saponaria* (*Handbuch*, viii. *Phytochem.* 15), (forming Henry & Boutron's *acrid principle*, Bley's *Quillaïn*) (Le Beuf); also in the bark of *Monina Polystachya* (*Handbuch, loc. cit.* 42), described by Mouchon (*N. Br. Arch.* 10, 178) as *Moninin*, recognised by Le Beuf as saponin. In the monesia-bark of *Chrysophyllum glycyphleum* (*Handbuch, loc. cit.* 63), Derosne, Henry & Payen (*J. Pharm.* 27, 28) found *Monesin*, which is identical with saponin. — In the following *Silenæ: Dianthus Caryophyllus, D. Carthusianorum, D. Cæsius,* and *D. prolifer; Lychnis chalcedonica, L. vespertina* and *L. Flos Cuculi. Silene inflata* and *S. nutans* contain saponin, the latter considerable quantities of it, but not in the seed (Malapert). — In the root of *Anagallis arvensis* and *A. cærulea* (Malapert).

Senegin or *Polyyalin*, discovered by Gehlen, in the root of *Polygala Senega*, which was associated with saponin by Buchholz and Pfaff, minutely examined by Quevenne, who named it *acide polyyalique,* and compared it with saponin, is, according to Bolley, probably identical with saponin. But Bolley did not follow Quevenne's mode of preparation, and moreover, did not operate on pure senegin. For this reason the two bodies are here treated as distinct, although the identity of their decomposition-products is regarded as established. Peschier's *polygalic acid* (*Repert.* 11, 2; 12, 430; 13, 457) was perhaps malic acid. The nature of Reinsch's *polygamarin* (*Repert.* 67, 305) from *Polygala amara* remains to be determined by further investigations.

The fruit of the horse-chestnut (*Handbuch*, viii, *Phytochem.* 25) contains saponin, according to Fremy, also according to Tipp (*Pharm. Vierteljahrsschr.* 3, 19); according to Rochleder (*Handbuch*, viii, *Phytochem.* 26), it contains a substance resembling saponin. Malapert found saponin in the ovaries during the flowering season, in the pericarp of the fruit, immediately after the fall of the petals; only a trace in the pericarp of the ripe fruit.

Saponin is contained in *Arnica montana* (*Handbuch, loc. cit.* 66) according to Buchholz; in *Arum maculatum* (*loc. cit.* 83), according to Enz (*Pharm. Viertelj.* 81, 27); in *Capsella Bursa Pastoris* (*Handbuch, loc. cit.* 38), according to Daubrawa (*Pharm. Viertelj.* 3, 337); in the bark of *Gymnoclodeis canadensis,* according to Braconnot (*Ann. Chim. Phys.* 50, 382; *Handbuch, loc. cit.*); in the root of *Polypodium vulgare,* according to Pfaff. Wahlenberg suspects its existence in the fruit of *Sapindus Saponaria* (*Handbuch, loc. cit.* 26), *S. laurifolius* and *S. rigidus;* Rochleder & Schwarz suppose it to exist in the fruit of *Pircunia abyssinica,* and in many plants of the sapindaceous and mimoseous orders.

The *irritating extractive matter* (*kratzender Extractivstoff*) found by Hünefeld (*J. pr. Chem.* 7, 57) in the root of the cowslip, *Primula veris* (*Handbuch, loc. cit.* 63), is perhaps identical with saponin.

Preparation. A. *From the root of Saponaria* or of *Gypsophila Struthium.* 1. The chopped root is exhausted with boiling alcohol of sp. gr. 0·824; the filtrate is cooled; and the deposit of saponin which separates after 24 hours is collected, washed with ether and alcohol, and dried at 100° (Rochleder & Schwarz). Overbeck treats the alcoholic solution with animal charcoal. — Schrader exhausted the aqueous extract with warm

alcohol, or the alcoholic extract with water. — If the root be boiled with weak spirit, the decoction concentrated and mixed with absolute alcohol, saponin is obtained, contaminated with gum or sugar. — 2. The coarsely-pounded root is freed by ether from resin and fat, then boiled with alcohol, and the flocks which separate on cooling and concentration are collected (Bley & Bussy).

B. *From Quillaia-bark.* This is the best material for preparing saponin for technical purposes (Le Beut). The same process as in A. 1 (Le Beuf); or the aqueous extract is boiled with alcohol; the liquid is filtered at the boiling heat, and the white flocks which fall down on cooling and concentration are purified by solution in alcohol, with aid of animal charcoal (Henry & Boutron, Bley).

C. *From the seeds of the Corn-cockle (Agrostemma Githago).* — 1. The coarsely pulverised dry seeds are freed from fixed oil by repeated exhaustion with ether, then by once exhausting with cold alcohol of 92° Tralles; the residue is boiled several times with alcohol of 84 Tr.; the liquid filtered at the boiling heat, and the saponin which separates on cooling is collected, an additional quantity being obtained by mixing the mother-liquor with absolute alcohol. The whole of the saponin thus obtained is dissolved in water; the solution is filtered to separate vegetable gelatin, then precipitated with neutral acetate of lead; the precipitate removed; the filtrate precipitated with basic acetate of lead; the latter precipitate, after thorough washing, decomposed under water by hydrosulphuric acid; and the limpid filtrate evaporated to dryness, or precipitated with absolute alcohol (Scharling). — 2. The aqueous extract of the seed is precipitated with sulphate of copper; hydrosulphuric acid is passed through the filtrate; the liquid again filtered, then digested with carbonate of baryta; the resulting baryta-salts precipitated by alcohol and separated by filtration; and the filtrate either strongly concentrated—in which case the saponin is to be precipitated by absolute alcohol,—or evaporated to dryness, and the residue boiled with alcohol of 93° Tr. Saponin thus prepared contains a small quantity of baryta (Scharling). — 3. Crawfurd digests the pulverised seeds with warm aqueous alcohol, evaporates the liquid to a syrup, mixes it with wood-charcoal, and dries it completely. The saponin is extracted from the residue by boiling with alcohol.

D. *From Horse-chestnuts.* The pulverised seeds are exhausted with cold alcohol, and the alcohol is distilled off from the tinctures. The yellowish jelly which remains consists, for the most part, of saponin, mixed with fat, a bitter crystallisable substance, and yellow-colouring matter; the fat may be removed by exhaustion with ether (Fremy).

Purification. Saponin prepared from *Gypsophila* by the first process is sometimes contaminated with foreign substances, probably in consequence of a peculiar constitution of the root, not indicated by any alteration of its outward appearance, in consequence of which the analysis shows too small an amount of carbon and of hydrogen. It is purified by dissolving it in the smallest possible quantity of water, and adding baryta-water, which precipitates saponin-baryta, leaving the foreign substances in solution. The white precipitate is washed with baryta-water and dissolved in water; on passing carbonic acid through the solution and heating it, carbonate of baryta separates

out, and after its removal the saponin may be precipitated by ether-alcohol (Rochleder & v. Payr).

Properties. White, non-crystalline, friable powder (Bussy, Henry & Plisson, Overbeck). Colourless (Rochleder & Schwarz); yellowish white (Quevenne). By precipitation of the concentrated aqueous solution with alcohol, it is obtained as a white starch-like mass; but when the alcohol is evaporated, it dissolves in the residual water to a syrup which dries up to a tough horny mass (Crawfurd, Scharling). Inodorous (Henry & Plisson); has a peculiar aromatic odour (Quevenne); inodorous when dry; the aqueous solution has a repulsive odour (Scharling). The dust excites violent sneezing. Saponin tastes sweetish at first, then burning and biting, and produces a persistent scratching sensation in the throat. — A drop of the aqueous solution introduced into the eye produces violent burning pain and dilatation of the pupil (Scharling). Neutral to vegetable colours. According to Quevenne it has an acid reaction. Acts poisonously on the smaller animals (Scharling).

Calculation according to Rochleder & Schwarz.

24 C	....	144	.... 52·17
20 H	....	20	.... 7·24
14 O	....	112	.... 40·59
$C^{24}H^{20}O^{14}$	....	276	.... 100·00

Calculations according to Overbeck.

42 C	....	252	.... 47·54
38 H	....	38	.... 7·16
30 O	....	240	.... 45·30
$C^{42}H^{38}O^{30}$	....	530	.... 100·00

According to Bolley.

36 C	....	216	.... 49·54
28 H	....	28	.... 6·42
24 O	....	192	.... 44·04
$C^{36}H^{28}O^{24}$	....	436	.... 100·00

Calculations according to Rochleder & v. Payr.

at 100°.

128 C	....	768	.... 52·97
106 H	....	106	.... 7·31
72 O	....	576	.... 39·72
$C^{128}H^{106}O^{72}$	....	1450	.... 100·00

at 100°, in vacuo.

128 C	....	768	.... 53·30
105 H	....	105	.... 7·29
71 O	....	568	.... 39·41
$C^{128}H^{105}O^{71}$	....	1441	.... 100·00

	Bussy.	Rochleder & Schwarz. at 100°.	Overbeck. *mean.* at 100°.	Bolley. *mean.*	Crawfurd.
C	50·0	52·54	46·81	49·10	50·72
H	7·4	7·26	7·51	6·88	7·44
O	42·6	40·20	45·68	44·02	41·84
	100·0	100·00	100·00	100·00	100·00

Rochleder & v. Payr.

	at 100°. *mean.*	at 100° *in vacuo.* *mean.*
C	52·64	53·17
H	7·37	7·57
O	39·99	39·26
	100·00	100·00

The saponin of Rochleder & Scharwz still contained small quantities of resin and

products of decomposition. Bolley's saponin contained about 1 p. c. ash, which is deducted. One sample of saponin examined by Rochleder & Schwarz contained 4·3 p. c. ash. In the other specimens the amount of ash is not stated. Rochleder formerly regarded the discrepancies in the analyses as the result of alterations which the saponin undergoes in drying; but he now regards saponin containing the smaller amount of carbon as impure; v. Payr, also found in saponin, before purification with baryta-water, 48·7 p. c. C. and 6·9 H. Respecting the formula see *Decomposition* 5. — Saponin is here, on the ground of Bolley's formula for sapogenin (xv, 53), enumerated among the glucosides with 24 at. C., although Rochleder & v. Payr's investigation assigns to it another, but still undetermined position.

Decompositions. 1. Saponin subjected to *dry distillation* swells up and gives off a large quantity of acid empyreumatic oil (Bussy). — 2. Aqueous saponin absorbs *oxygen*, and becomes turbid, giving off carbonic acid and depositing white elastic flocks (Schrader, Braconnot). When the solution is repeatedly evaporated it becomes darker (Buchholz). Alcoholic saponin set aside for a year in a loosely covered vessel once yielded needles which burnt away without ash. — 3. With *oil of vitriol* it forms a reddish-yellow solution, changing to bright red and ultimately to violet-red (Quevenne). It imparts to oil of vitriol a red-colour changing to violet-red when heated, and finally becomes charred (Bley). — 4. Saponin dissolved in 12 pts. of *chlorine-water* forms a brown turbid liquid, which in the course of 12 hours deposits white flocks soluble in alcohol (Buchholz, Braconnot). *Tincture of iodine* does not alter aqueous saponin (Bley). — 5. By dilute *mineral acids*, saponin is decomposed, slowly in the cold, more quickly when heated, into sapogenin (xv, 53) and a carbohydrate (Overbeck, Rochleder & Schwarz). Saponin from horse-chestnuts, heated with hydrochloric acid or subjected to the action of the electric current, deposits sapogenin immediately, and when merely set aside with hydrochloric acid it deposits that substance after a while, whereas saponin from *Saponaria* yields sapogenin only when heated (Fremy). — Saponin dissolves completely in cold concentrated hydrochloric acid, without tumefaction, the solution not yielding any precipitate on addition of water. When boiled with equal quantities of water and hydrochloric acid, it likewise dissolves without forming any gelatinous precipitate, but on addition of water, deposits white flocks of sapogenin (Quevenne). Saponin and sapogenin react in the same way with hydrochloric acid (Bolley). Acetic acid acts like hydrochloric acid, though more slowly, so that saponin cannot be freed from admixed ash by solution in alcoholic acetic acid.

Formulæ for the reaction: *a.* according to Rochleder & Schwarz, who regard the decomposition-product as identical with chinovin:

$$C^{24}H^{20}O^{14} = C^{12}H^9O^3 + C^{12}H^{11}O^{11};$$

b. According to Overbeck:

$$C^{42}H^{38}O^{30} = C^{18}H^{14}O^6 + C^{24}H^{24}O^{24};$$

c. According to Bolley:

$$2C^{36}H^{24}O^{20} + 10HO = C^{24}H^{18}O^{10} + 4C^{12}H^{10}O^{10}.$$
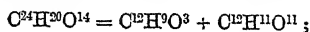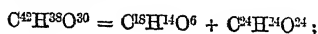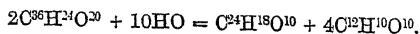
On the carbo-hydrate thus produced, see xv. 348, and below.

Saponin when decomposed by acids, is capable of yielding various products of decomposition, according as, of the 6 at. carbohydrate which it contains, two, more than two, or the whole are separated.

Of these products, the 'former are obtained by the action of aqueous acids, but complete decomposition is produced only by the action of alcoholic hydrochloric acid (Rochleder & v. Payr). According to this, only the crystals described under d are the true sapogenin, and the body described at page 53, vol. xv, must be regarded as a product of imperfect decomposition:

a. The product $C^{128}H^{106}O^{72}$, obtained from saponin by elimination of 2 at. carbohydrate, is perhaps Fremy's æsculic acid (xv, 54, anal. b.) as it agrees in amount of carbon with the formula $C^{104}H^{82}O^{48}$ (calc. 57·25 p. c. C. and 7 52 H.) (Rochleder).

b. Saponin purified with baryta-water yields, when heated with aqueous hydrochloric acid, 53·1 p. c. sugar and gelatinous flocks, which, when dried at 100° C., contain, on the average, 65 p. c. C. and 8·64 H., agreeing nearly with the formula $C^{80}H^{62}O^{28}$ (calc. 62 66 p. c. C. 8 09 H.). In this case the decomposition takes place chiefly in the manner shown by the equation:

$$C^{128}H^{106}O^{72} + 4HO = C^{80}H^{62}O^{28} + 4C^{12}H^{12}O^{12}.$$
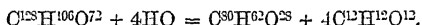
(calc. 49·62 p. c. $C^{12}H^{12}O^{12}$). Overbeck's sapogenin $C^{80}H^{61}O^{27}$ (xv, 54) likewise belongs to this place (Rochleder & v. Payr).

c. By prolonged boiling with aqueous hydrochloric acid, 62·66 p. c. sugar and a jelly $C^{68}H^{52}O^{18}$ are obtained (calc. 67·55 p. c. C. 8·61 H):

$$C^{128}H^{106}O^{72} + 6HO = C^{68}H^{52}O^{18} + 5C^{12}H^{12}O^{12}.$$
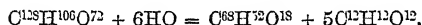
(Calc. 59·8 p. c. $C^{12}H^{12}O^{12}$.) This appears to be the composition of the sapogenin analysed by Rochleder & Schwarz (xv, 54, b).

d. When the flocks which separate on boiling saponin with aqueous hydrochloric acid, are dissolved in anhydrous alcohol, and hydrochloric acid gas is passed for several hours through the boiling solution, white crystals $C^{56}H^{42}O^8$ are deposited, produced by complete resolution of the saponin (Rochleder & v. Payr):

$$C^{128}H^{106}O^{72} + 8HO = C^{56}H^{42}O^8 + 6C^{12}H^{12}O^{12}.$$
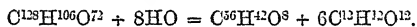
These crystals, after recrystallisation from alcohol and drying at 100°, contain on the average 75·78 p. c. C., 9·76 H., and 14·46 O (calc. for $C^{56}H^{42}O^8$, 76·02 p. c. C., 9 50 H., and 11·48 O.). They are insoluble in water, dissolve sparingly in cold, easily in hot alcohol, and are nearly insoluble in aqueous potash. From the easily produced solution in alcoholic potash, aqueous potash throws down almost the whole of the compound of sapogenin and potash, which gives up its potash during washing. (Rochleder & v. Payr.)

The carbohydrate produced, together with sapogenin, is insoluble in alcohol at the moment of separation, and is converted into dextroglucose only by the prolonged action of hot acids (Rochleder & v. Payr). See the preceding statements (xv, 348).

6. *Nitric acid* of sp. gr. 1·33 dissolves saponin easily, gives off red fumes when heated, and deposits a sulphur-yellow resin, and afterwards on cooling, white pulverulent mucic acid. Oxalic acid is likewise formed. (Crawfurd.) The solution of saponin in strong nitric acid deposits, on addition of water, xyloïdin and a very bitter substance (Braconnot, *Ann. Chim. Phys.* 52, 293). (See also Bussy, Henry & Plisson, Scharling, Fremy.)

7. When saponin from horse-chestnuts is treated with *potash-ley*, a compound of potash with a yellow colouring matter contained in the saponin is first formed, — afterwards sapogenin-potash (æsculate of potash), from the solution of which the sapogenin is thrown down by acids (Fremy). Saponin from saponaria treated in like manner does not yield sapogenin (Fremy). Aqueous saponin boiled with potash-ley, then mixed with hydrochloric acid, yields a white tolerably abundant non-gelatinous precipitate of sapogenin (Quevenne). Saponin mixed with potash-ley and evaporated turns brown, and the residue forms with water, a brown solution from which acids do not precipitate Fremy's æsculic acid (Rochleder & Schwarz). By the action of potash upon saponin, a finely crystallised acid and an amorphous substance are obtained, the latter being resolved by hydrochloric acid into two products (v. Payr & Rochleder, *Wien. Akad. Ber.* 24, 42).

8. Saponin boiled with an alkaline solution of *cupric oxide*, throws down a small quantity of cuprous oxide (Bolley). According to Scharling, it forms with cupric sulphate and potash, a blue-green precipitate, without reducing the cupric oxide.

Combinations. Dried saponin is very slightly hygroscopic. (Scharling.) — It dissolves easily in *water*, a solution containing $\frac{1}{1000}$ of saponin, forming a frothy liquid (Schrader, Bussy and others). With a small quantity of water it swells up to an opaque hydrate, but recovers its transparency when thoroughly dry. (Henry & Plisson.)

Aqueous saponin is not altered by cold dilute *acids* (Bussy), and does not unite with them.

It dissolves sparingly in cold aqueous *ammonia* and *potash*, more freely in the same liquids when warm (Bley). Alkalis and lime-water do not precipitate saponin from its aqueous solution (Bussy), but colour the liquid yellow (Buchholz, Braconnot), so likewise do ammonia (Dulong), and carbonate of potash (Trommsdorff).

The solution of 1 pt. saponin in 4 pts. water throws down from *baryta-water*, a white precipitate soluble in excess of saponin or of baryta-water (Bussy). The compound is insoluble or nearly so in baryta-water, but dissolves easily in pure water (Rochleder & v. Payr).

Aqueous saponin does not precipitate any *metallic salt* (Braconnot).

With solution of *neutral acetate of lead* aqueous saponin forms a gelatinous precipitate. On boiling the filtrate, a further precipitate of pulverulent character is obtained which swells up during washing (Rochleder & Schwarz). The precipitate is soluble in acetic acid. (Buchholz.) According to Braconnot and Bussy, neutral acetate of lead does not precipitate solution of saponin.

Basic acetate of lead, added to aqueous saponin throws down a copious precipitate (Bussy); curdy (Henry & Boutron).

Ferric chloride colours aqueous saponin pale olive-green, and after some time throws down light grey flocks (Buchholz).

Alcoholic saponin does not precipitate *nitrate of silver* (Scharling).

Saponin dissolves in dilute, more easily than in strong *alcohol*, and is insoluble in absolute alcohol (Schrader and others). The solution does not froth. It dissolves in 400 pts. absolute alcohol (Bley). Its solubility in alcohol is increased by the presence of hydrochloric or

acetic acid (Bussy). A concentrated aqueous solution of saponin is not precipitated by alcohol (Crawfurd).

Saponin is insoluble in *ether* and in *volatile oils*. It does not precipitate solution of gelatin (Trommsdorff). According to Braconnot and Dulong, it precipitates *tincture of galls* in greyish yellow flocks; according to Scharling, only when it is impure.

Osborne's *Principle of Saponaria officinalis.* — Occurs in the roots only before flowering time. Obtained from the aqueous decoction. Whitish radiate needles, which melt at a moderate heat. Extremely bitter. Neutral. — Swells up and blackens in the *fire;* carbonised by *oil of vitriol.* — Dissolves in less than 2 pts. *water;* soluble in *alcohol,* and in *ether,* insoluble in *oil of turpentine* (Osborne, *Ann. Phil.* 11, 302; *Kastn. Arch.* 8, 293; *Berl. Jahrb.* 1827, 2, 147; *Berz. Jahresber.* 7, 269.

Senegin.

GEHLEN. *Berl. Jahrb.* 1804, 112.
J. DULONG. *J. Pharm.* 13, 567.
TROMMSDORFF. *N. Tr.* 24, 2, 28.
QUEVENNE. *J. Pharm.* 22, 460; abstr. *Ann. Pharm.* 20, 34; *J. Pharm.* 23, 270.
BOLLEY. *Ann. Pharm.* 90, 211; abstr. *J. pr. Chem.* 63, 92. — *Ann. Pharm.* 91, 117; abstr. *J. pr. Chem.* 63, 253.
W. PROCTER, jun. *Chem. News,* 1861, 40; *Zeitschr. Ch. Pharm.* 4, 153.

Polygalin, Acide polygalique. Found, together with resin, by Gehlen in the root of *Polygala Senega,* and described as a substance perfectly insoluble in water and ether, but soluble in alcohol. Associated, by Pfaff, who called it *kratzender Extractivstoff,* and by Bucholz, who named it *Senegin,* with saponin, which is soluble in water. Dulong was not able to obtain Gehlen's senegin, but he prepared from senega-root a product agreeing with Gehlen's resin, which he designated as *matière acre,* agreeing in some respects with saponin. Pure senegin appears to have been first obtained by Quevenne, according to whom it is different from saponin, whereas Bolley, who however did not follow Quevenne's mode of preparation, regards the two as identical. — According to A. Vogel (*N. Repert.* 6, 289), picrolichenin (xv, 55) is identical or at least isomeric with senegin.

Preparation. From Senega-root. 1. The root is exhausted with cold water; the extract concentrated, and filtered from the separated flocks containing senegin and earthy salts; the filtrate precipitated with neutral acetate of lead; the liquid again filtered, freed from lead by hydrosulphuric acid, and evaporated to an extract; this extract exhausted with alcohol of 36°; the tincture evaporated; the residue freed by ether from yellow colouring matter and fat, then dissolved in water; the solution precipitated with basic acetate of lead, and the precipitate washed and decomposed by hydrosulphuric acid. Part of the senegin then remains with the sulphide of lead, while another portion dissolves, so that: *a.* The sulphide of lead is collected and boiled with alcohol; *b.* The liquid filtered from the sulphide of lead is evaporated to dryness, and the residue is boiled with alcohol. The hot-filtered tinctures cooled and left to evaporate, deposit senegin, which may be purified, if necessary, by re-solution in alcohol and treatment with animal charcoal (Quevenne). Senega-root exhausted with water still yields senegin when boiled with alcohol, the tincture depositing the senegin when cooled or concentrated. It

is purified from fat by ether, then with basic acetate of lead, as above (Quevenne). — 2. Bolley precipitates the aqueous solution of officinal extract of senega with neutral acetate of lead; collects and washes the precipitate; decomposes it with hydrosulphuric acid; evaporates the filtrate to dryness; boils the residue with alcohol; evaporates the tincture; treats the residue with ether; dissolves the portion not taken up by the ether in water; precipitates the solution with basic acetate of lead; decomposes the thoroughly washed precipitate under water with hydrosulphuric acid; evaporates the filtrate; and purifies the senegin which remains by repeated solution in boiling alcohol and cooling. Bolley supposes this process to be the same as that of Quevenne, but the two methods differ in this respect, that Quevenne obtains the senegin from the filtrate after precipitation with acetate of lead, whereas Bolley obtains it from the precipitate itself. This precipitate, according to Quevenne, contains only traces of senegin (Kr.). — 3. The pulverised root is exhausted with alcohol of 33°; the greater part of the alcohol is distilled off; the residual syrup is freed from fat by ether: the deposit formed after standing for some time is collected and suspended in water; the turbid filtrate is mixed with a little alcohol which facilitates the formation of a precipitate; and the liquid is left to itself for several days. The deposit which then forms is collected and purified by solution in warm alcohol with help of animal charcoal: the filtrate, as it cools, deposits senegin. The liquid decanted from the sediment still contains a small quantity of senegin, which may be obtained, as in method 1, by precipitation with basic acetate of lead (Quevenne). — 4. Pulverised senega root is exhausted with a mixture of 2 pts. alcohol and 1 pt. water, the tincture is concentrated, and the residue repeatedly shaken up with ether as long as the ether becomes coloured by it. The residual syrup set aside for some time with a mixture of 3 pts. alcohol and 1 pt. ether, and frequently shaken, deposits senegin as a nearly colourless precipitate, which is to be washed with ether-alcohol, pressed between paper, and dried[1] It is purified by solution in boiling water, precipitation with ether-alcohol, re-solution in boiling alcohol, and decoloration with animal charcoal (Procter).

Older processes. Gehlen treats the alcoholic extract of senega-root with ether to free it from soft resin, then with water to remove a sweet and an acrid substance. Dulong, in repeating this process, found that ether dissolved a portion of the extract, and water the rest; but Trommsdorff obtained a product agreeing, to a certain extent, with Gehlen's senegin. See Dulong's directions for preparing the resin and the acrid extractive matter (*J. Pharm.* 13, 572).

Properties. Senegin which separates from the alcoholic solution on cooling, is a white powder; when obtained by evaporating the aqueous solution, it forms opaque, greenish-white scales (Quevenne). Nearly white powder with a greyish yellow tint (Bolley). Permanent in the air. Smells like saponin, but fainter. Tastes like saponin, which it likewise resembles in exciting violent sneezing, even in the smallest quantity. Reddens litmus (Quevenne, Gehlen). Poisonous (Quevenne).

					Quevenne. mean.		Bolley. mean, at 100°.
36 C	216	......	54	....	54·62	......	53 58
24 H	24	....	6	....	7·53	....	6·23
20 O	160	....	40	... ...	37·85	.	40·19
$C^{36}H^{24}O^{20}$	400	....	100	....	100·00	... .	100·00

So, according to Bolley; according to Quevenne, it is $C^{22}H^{18}O^{11}$; according to Delffs (*N. Jahrb. Pharm.* 11, 356), it is $C^{28}H^{20}O^{14}$. — Quevenne's analyses have been recalculated on the supposition that he took $C = 76.5$. Bolley's senegin contained 1.13 p. c. ash, which has been deducted in the calculation.

Decompositions. 1. Slightly decomposed by heating to 200°, completely at a stronger heat (Quevenne). — 2. When heated on platinum-foil it burns with a smoky flame, leaving a light, easily combustible charcoal (Quevenne). Gehlen's senegin does not melt in the fire, but swells up, takes fire, burns with a smell of burnt tartar, and leaves charcoal. — 3. With *oil of vitriol* it behaves like saponin [(Quevenne). — 4. When senegin is diffused through 30 pts. of strong *hydrochloric acid*, it swells up like gum tragacanth and forms a greenish jelly of sapogenin. Boiling concentrated hydrochloric acid carbonises it partially, with more rapid formation of a jelly; more dilute acid gelatinises it only on boiling (Quevenne). An aqueous solution of senegin heated with dilute sulphuric acid, becomes turbid, deposits white flocks, and is resolved into sapogenin and a sweet substance, which reduces cupric oxide in alkaline solution (Bolley). The aqueous solution is not altered by oxalic, citric, or acetic acid (Quevenne). — 5. Senegin dissolves with yellow colour in strong *nitric acid*, the solution when heated yielding oxalic acid and a pale yellow substance, which, after washing with water, has a harsh and bitter taste (Quevenne). With nitric acid it forms picric and oxalic acids (Procter). It forms with nitric acid a turbid solution, which partly coagulates to a jelly when heated (Gehlen.) — 6. Aqueous senegin is decomposed by boiling with *caustic potash*, and on subsequent addition of hydrochloric acid deposits a jelly (Quevenne). — When boiled with an alkaline solution of *cupric oxide*, it exhibits an indistinct separation of cuprous oxide.

Combinations. Senegin dissolves slowly in cold, quickly (more abundantly, according to Bolley) in hot *water*. The solution froths up strongly when agitated (Quevenne). According to Gehlen, it is quite insoluble in water.

According to Quevenne and Procter, senegin unites with bases, forming the salts called *Polygalates*. Aqueous senegin does not expel carbonic acid from alkaline carbonates or hydrosulphuric acid from hydrosulphates, even with the aid of heat. It assumes a greenish colour when neutralised with alkalis, and leaves greenish transparent films when evaporated (Quevenne). The solution of senegin in soda-ley is precipitated in white flocks by acids (Trommsdorff, vid. sup.). From the aqueous infusion of senega-root, senegin may be precipitated by acids, but it redissolves partially during washing (Buchner, *Repert.* 88, 176).

Baryta-water added to aqueous senegin throws down a copious white precipitate, but the solution of senegin in potash-ley does not precipitate chloride of barium (Quevenne). — Senegin forms a soluble compound with *magnesia* (Quevenne).

A small quantity of *neutral acetate of lead* produces in aqueous senegin a slight turbidity, which disappears on the addition of a larger quantity. The compound of senegin and magnesia forms a white precipitate with neutral acetate of lead. Aqueous senegin precipitates *basic acetate of lead* (Quevenne).

Aqueous senegin forms a precipitate with *mercurous nitrate*, but not

with mercuric chloride, or with ferric, cupric, or silver salts, not even with tartar-emetic.

Senegin is more soluble in aqueous than in absolute *alcohol*, and more in hot than in cold alcohol (Gehlen, Bolley). It dissolves in all proportions in boiling absolute alcohol, and partly separates out on cooling (Quevenne).

It is insoluble in common *ether, acetic ether*, and *oils*, both *fixed* and *volatile* (Gehlen, Quevenne).

Aqueous senegin forms a dirty white precipitate with *tincture of galls* (Quevenne).

Yellow Colouring matter of Senega.   When the aqueous extract of senega is precipitated by basic acetate of lead, the filtrate evaporated after being freed from lead by hydrosulphuric acid, and the residue treated with ether, the ether takes up a yellow colouring matter, which remains behind on evaporation. — Yellow-brown scales, which melt at 160°, are inodorous and very bitter.   Reddens litmus.

Does not give off ammoniacal vapours by *dry distillation.   Burns* with a dense flame. — Is coloured brown-red by *oil of vitriol.*

Dissolves sparingly in *water*, easily and with yellow colour in *ammonia, potash*, and *soda.*   Forms coloured precipitates with *metallic salts.* — Soluble in *alcohol* and in *ether* (Quevenne, *J. Pharm.* 22, 467).

Glucosides with unknown Copulæ.

1: Apiin.

BRACONNOT.   *N. Ann. Chim. Phys.* 9, 250.
v. PLANTA & WALLACE.   *Ann. Pharm.* 74, 262.

Discovered by Braconnot in parsley; occurs in small quantities in celery.

Preparation.   Fresh parsley, gathered before flowering is boiled three times with water; the liquid is strained through linen; and the dark green jelly which forms on cooling is washed with cold water and dried over the water-bath.   The dirty-green residue is repeatedly treated with boiling alcohol, as long as the tincture runs off green; the solution is mixed with water, and so much of the alcohol is distilled off, that the remaining liquid solidifies to a thick green paste, mixed with a white powder, which is freed from the liquid by straining and pressure.   The greenish-white substance left on the cloth is repeatedly dipped, together with the cloth, into warm alcohol, then pressed and freed from soluble matter by boiling with ether.   Apiin thus obtained still retains a small quantity of ash. — A certain quantity of apiin still remains dissolved in the alcoholic mother-liquor, whence it may be obtained by concentration and purifying the substance thus separated with ether (v. Planta & Wallace).

Braconnot boiled parsley with water, strained it while still at the boiling heat, and washed the jelly which separated on cooling with cold water.   This process does not yield pure apiin (v. Planta & Wallace).

Properties. Soft white powder destitute of taste and smell, melting without loss at 180°, and solidifying to a yellow brittle glass. Neutral.

Calculation according to v. Planta & Wallace.				v. Planta & Wallace.		
24 C	144		54·96	54·71	to	55·25
14 H	14		5·34	5·60	,,	5·59
13 O	104		39·70	39·69	,,	39·16
$C^{24}H^{14}O^{13}$	262		100·00	100·00		100·00

After deduction of 0·15 and 0·36 p. c. ash. It doubtless belongs to the glucosides (or perhaps to the mannitanides), a circumstance which throws doubt on the formula proposed by v. Planta & Wallace.

Decompositions. 1. Apiin *heated* above its melting point, swells up and becomes carbonised; if the carbonisation is only partial, the rest of the substance remains unaltered (Braconnot). It begins to decompose at 200°—210° (v. Planta & Wallace). By dry distillation it yields an acid product (Braconnot). — 2. When heated in contact with the air it burns with flame. — 3. The solution in boiling water, which is faintly yellowish at first, becomes darker coloured by continued boiling, finally reddish yellow, and on cooling deposits nearly colourless flocks, without production of a jelly. The solution evaporated to dryness leaves a residue, the weight of which, increased by assumption of water, amounts to 112·28 pts. for every 100 pts. of apiin employed. This residue is brittle, crumbles to a brown powder, and contains 50·98 p. c. C., 6·03 H., and 43·09 O. It dissolves in boiling water; does not solidify to a jelly on cooling; does not melt before decomposing when heated; is precipitated by neutral acetate of lead; and still exhibits with ferrous sulphate the blood-red colour produced by apiin. v. Planta & Wallace assign to this product the formula $C^{24}H^{16}O^{15}$. — 4. When *chlorine gas* is passed into the aqueous jelly of apiin, a yellow chlorinated product is formed, insoluble in boiling water, soluble in alcohol and in aqueous alkalis (Braconnot). The dirty yellow precipitate formed on passing chlorine gas into hot aqueous apiin, appears dark brown after drying and trituration, and burns when heated, emitting an odour of hydrochloric acid. It dissolves easily in warm water, forming a frothy neutral solution, which deposits yellow flocks on cooling, exhibits with ferrous sulphate the blood-red colour of apiin, and is precipitated by neutral acetate of lead (v. Planta & Wallace). — 5. Apiin treated with *nitric acid* yields a large quantity of picric, and a trace of oxalic acid (Braconnot). v. Planta & Wallace did not obtain either of these acids by boiling pure apiin with nitric acid; but impure apiin yielded orange-yellow detonating nodules and a large quantity of oxalic acid. — 6. Apiin heated with *peroxide of manganese* and *dilute sulphuric acid* gives off carbonic, formic and acetic acids (v. Planta & Wallace).

7. Apiin dissolves in *oil of vitriol*, forming an orange-red solution which blackens when heated, and gives off sulphurous acid. From the solution in cold oil of vitriol, water separates a large quantity of yellow flocks, which appear yellowish brown after drying, dissolve sparingly in water, and gelatinise to a certain extent. These flocks contain 59·06 p. c. C., 5·08 H. and 35·86 O., corresponding, according to v. Planta & Wallace, with the formula $C^{24}H^{12}O^{11}$. — *Strong hydrochloric*

acid acts like oil of vitriol, and on heating the liquid, dark brown flocks are separated.   When hydrochloric acid gas is passed over apiin dried at 100°, the apiin assumes a deep yellow colour, and increases in weight by 5·12 per cent. (v. Planta & Wallace).

A hot aqueous solution of apiin boiled for some time with *dilute acids*, becomes turbid, and thickens to a yellowish pulp, which, when washed on the filter, leaves a light yellow mass, which separates from its solutions, no longer as a jelly, but as a white deposit, and forms blood-red flocks with ferrous sulphate.   The liquid which runs off is found, after neutralisation with chalk, to contain a certain quantity of sugar (Braconnot).   The white flocks which separate on boiling apiin with dilute sulphuric or hydrochloric acid, dry up, after washing, to a light-brown mass, which has the same composition, whichever of the two acids is employed, and whether the boiling is continued for a short time only or for a day, viz., on the average 63·45 p.c. C., 4·52 H., and 32·03 O.   These flocks dissolve very sparingly in boiling water, and separate again, on cooling, in the form of white flocks; they dissolve readily in boiling alcohol, and form a red-brown precipitate with ferrous sulphate. Those prepared with hydrochloric acid dissolve more easily in boiling water, forming a yellowish solution which does not gelatinise on cooling. The solution filtered from the flocks and freed from sulphuric acid by carbonate of baryta, leaves a sweetish syrup, probably containing remains of the flocks and sugar.

Combinations. — With water.   Apiin dried over oil of vitriol gives off at the heat of the water-bath, 4·21 p. c. water, which it absorbs again from the air in the course of a night (v. Planta & Wallace).   It dissolves easily in boiling water, forming a clear liquid (especially after fusion, according to v. Planta & Wallace), which immediately gelatinises on cooling, or on addition of cold water (Braconnot).   A solution containing only 1 pt. apiin in 1,500 pts. water yields a loose jelly on cooling (v. Planta & Wallace).

It dissolves easily, especially in the gelatinous state, in aqueous *ammonia* and *alkaline bicarbonates*, forming yellowish solutions, which yield gelatinous precipitates with acids.   No decomposition takes place, even after continued boiling with potash-ley, the orange-red solution still gelatinising when neutralised with an acid (Braconnot, v. Planta & Wallace).   It dissolves in *lime-water*, completely according to Braconnot, partially according to v. Planta & Wallace.

Apiin is not precipitated from its aqueous or alcoholic solution by aqueous *chloride of barium, neutral acetate of lead,* or *nitrate of silver.* An alcoholic solution of neutral acetate of lead forms with alcoholic apiin a deep yellow precipitate, containing from 53·6 to 61·1 p. c. lead-oxide (v. Planta & Wallace).

The solution of apiin in boiling water is coloured deep blood-red by *ferrous sulphate*, even when very dilute.

Apiin dissolves in boiling *alcohol*, and solidifies to a jelly on cooling (Braconnot).   It dissolves in 390 pts. of cold alcohol (v. Planta & Wallace).   The hot aqueous solution mixed with *tincture of galls* solidifies on cooling to a white opaque jelly, which becomes liquid again when heated (Braconnot).

2. Cnicin.

NATIVELLE. *J. Chim. méd.* 21, 69.

FR. SCRIBE. *Compt. rend.* 15, 802; *J. pr. Chem.* 29, 191; *Ann. Pharm.* 44, 289.

DESSAIGNES & CHAUTARD. *N. J. Pharm.* 21, 26; *N. Repert.* 1, 219.

Centaurin. Carduibenedictenbitter Discovered in 1839 by Nativelle in the leaves of *Cnicus benedictus* (*Handb.* viii. *Phytochem.* 68). It occurs also in *Centaurea Calcitrappa* and many other *Cynarocephalæ.* — On an amorphous bitter substance from *Cnicus benedictus,* see Morin (*J. Chim. méd.* 3, 108). On an amorphous acid, *Calcitrappic acid,* from *Centaurea Calcitrappa,* see Calignon (*N. Br. Arch.* 83, 186).

Prepared like salicin (Nativelle). Probably therefore by precipitating the decoction with neutral acetate of lead, filtering, separating the lead by hydrosulphuric acid, evaporating, and decolorising with animal charcoal (Kr).

Transparent colourless needles having a silky lustre. Inodorous with a strong bitter taste. Permanent in the air. Neutral. Fusible, but not volatile without decomposition (Scribe). — Dextrorotatory, $[\alpha]r = 130.68°$ (for cnicin dried over quicklime at mean temperature). The addition of 1 p.c. hydrochloric acid reduces the deflection by one-fifth; if the solution be then supersaturated with soda, it acquires a faint colour, loses its bitter taste, and half of its still remaining rotatory power, which is only partially restored by addition of hydrochloric acid. (Bouchardat, *Compt. rend.* 18, 299; *J. pr. Chem.* 32, 91.)

Calculation according to Scribe.				Scribe. mean.	Dessaignes & Chautard.
42 C	252	63		62·9	62·9
28 H	28	7		7·0	6·8
15 O	120	30		30·1	30·3
$C^{42}H^{28}O^{15}$	400	100		100·0	100 0

The formulæ $C^{28}H^{18}O^{10}$, $C^{40}H^{26}O^{14}$, $C^{52}H^{34}O^{18}$, and others, likewise require numbers agreeing with the analyses (*Handw.* 2 Aufl. 2 [2], 799).

Decompositions. Cnicin decomposes when strongly *heated,* becoming yellow and resinous, takes fire, burns with a white flame, and leaves a tumefied charcoal which burns away without residue. — It dissolves with bright red colour in *oil of vitriol,* the solution turning black when heated. The cold solution turns violet when mixed with water, and yellow on subsequent addition of ammonia. — Cold concentrated *hydrochloric acid* dissolves cnicin with green colour; the solution turns brown when heated, and becomes turbid from separation of oil-drops, which, on cooling, form a yellow resin (Scribe).

Cnicin is nearly insoluble in cold *water,* but much more soluble in boiling water. The solution turns brown when boiled for some time, and on cooling deposits a thick turpentine-like oil.

Cnicin dissolves in all proportions in *wood-spirit* and in *alcohol,* scarcely in *ether,* not at all in *oil of turpentine* or in *fixed oils* (Scribe).

3. Lycopodium-bitter.

KAMP & BOEDEKER (1856). *Ann. Pharm.* 100, 300; abstr. *J. pr. Chem.*
70, 371.

In *Lycopodium Chamæcyparissus.* An alcoholic extract is first prepared
from the herb, then an aqueous extract from the residue; the aqueous
solutions of both are precipitated successively by neutral and by basic
acetate of lead; and the filtrate, freed from excess of lead by hydro-
sulphuric acid, is evaporated.   The residue exhausted with alcohol
gives up glucose to that solvent, while the bitter remains behind and
may be dissolved in water and precipitated by basic acetate of lead.
The precipitate is decomposed under water by hydrosulphuric acid, the
the solution freed from the sulphide of lead is fermented with yeast,
evaporated after the fermentation is ended, and exhausted with abso-
lute alcohol.   The alcohol then takes up the bitter, and when evapo-
rated, leaves a syrup mixed with colourless needles. — It is not very easy
to see why the bitter should be precipitable by basic acetate of lead, and soluble in
absolute alcohol in the latter stage of the process, whereas in the former it exhibits
exactly opposite properties. Kr.

Has a very bitter and nauseating taste. Neutral. Free from
nitrogen. — *Oil of vitriol* colours it deep red at first, then brown.   In
very dilute aqueous solution it forms with *tincture of iodine* a deep
scarlet precipitate; in more concentrated solutions, a red-brown pre-
cipitate.   It reduces cuprous oxide from an *alkaline cupric solution,* not
immediately, but after boiling with dilute sulphuric acid.   From
nitrate of silver it throws down a white precipitate, which turns black
on boiling.

Soluble in *water, alcohol* and *ether.*

Appendix to Lycopodium-bitter.

a. Lycostearone.

KAMP & BOEDEKER.   *Ann. Pharm.* 100, 302.

In *Lycopodium Chamæcyparissus.* Separates from the alcoholic tinc-
ture of the herb on evaporation; and by washing with cold alcohol and
water, and repeated solution in boiling alcohol, with aid of animal
charcoal, it is obtained on cooling as a jelly, which dries up to an
amylaceous mass.

Amorphous, inodorous and tasteless mass, which melts partially at
75°, completely at 100°.   Neutral.

Approximate calculation.					Kamp.
30 C	180	....	74·38	....	74·15
30 H	30	....	12·40	....	12·63
4 O	32	....	13·22	....	13·22
$C^{30}H^{30}O^4$	242	....	100·00	....	100·00

When heated, it *burns* with an odour of fat. — With cold *oil of*
vitriol, it turns brown, with hot oil of vitriol, black; with boiling *nitric*

acid, rcd. It is insoluble in cold, sparingly soluble in boiling *water*, easily in *alkalis* and *alkaline carbonates*, and is precipitated therefrom by acids. — Dissolves sparingly in cold *alcohol* and *ether*, abundantly at the boiling heat.

b. Lycoresin.

KAMP & BOEDEKER (1856). *Ann. Pharm.* 100, 303.

In *Lycopodium Chamæcyparissus*. — The mother-liquors remaining after the separation of lycostearone (*vid. sup.*) are evaporated, the residue is treated with water, and the undissolved portion is boiled with a small quantity of soda-ley. The liquid on cooling, deposits lycoresin, which may be recrystallised from boiling alcohol.

Properties. Microscopic, four-sided prisms with oblique end face. Neutral.

					Kamp. *mean.*
36 C	....	216	....	77·14	.... 77·04
32 H	....	32	....	11·43	.... 11·22
4 O	....	32	.... .	11·43	... . 11·74
$C^{36}H^{32}O^4$	.. ..	280	....	100·00	.... 100·00

Heated to about 170°, it melts, decomposes, and *burns* like resin. — Colours *oil of vitriol* orange, then brown. — By aqueous *alkalis* it is dissolved sparingly in the cold, and decomposed when heated.

Insoluble in *water*. — With most *metallic salts* it forms no precipitate, with an alcoholic solution of *mercuric chloride*, a white precipitate.

Dissolves abundantly in *alcohol* and *ether*.

4. Pariglin.

PALLOTTA. *Brugn. Giorn.* 17, 386; *Schw.* 44, 147; *N. Tr.* 10, 2, 120; *Mag. Pharm.* 9, 140.

THUBEUF. *J. Pharm.* 18, 734; *Schw.* 67, 282; *J. Pharm.* 20, 162 and 679.

BATKA. *Ann. Pharm.* 11, 313. — *J. Pharm.* 20, 43.

POGGIALE. *J. Pharm.* 20, 553; *J. Chim. méd.* 10, 577; *Ann. Pharm.* 13, 84.

CHR. PETERSEN. *Ann. Pharm.* 15, 74; 17, 166.

Discovered in 1824 by Pallotta, designated by Folchi as *Smilacin*, by Thubeuf, in 1831, as *Salseparin*, by Batka as *Parillic acid*. Poggiale showed that the modes of preparation adopted by these several chemists yield the same substance. Buchner (*Repert.* 53, 1), regarded pariglin as identical with chinovin, which view was however refuted by Petersen's analysis.

Occurrence. In sarsaparilla root (*Handbuch*, viii. *Phytochem.* 85), more abundantly in the bark than in the inner part.

By boiling the bark of *Smilax China* (*Handbuch*, viii. *Phytochem.* 86) pulverised and exhausted with ether, with alcohol of 75 p. c., eva-

porating the tincture, and pouring water on the residue, Reinsch obtained his *Smilachin*, which at first separated in flocks and was afterwards converted into crystalline laminæ. This substance is tasteless, neutral, and yields, with water, a solution which froths like soap-suds. Reinsch at first regarded it as identical with, afterwards as different from, salseparin. (Comp. *Repert.* 82, 145; abstr. *Jahrb. pr. Pharm.* 8, 41; further *Jahrb. pr. Pharm.* 8, 291; 9, 109.)

The name *Smilasperic acid* was given by Garden (*Lond. Med. Gaz.* 20, 809; abstr. *Repert.* 66, 268) to crystals which were obtained from the extract of the Italian sarsaparilla of *Smilax aspera* [more correctly according to Buchner, Jun. (*Repert.* 71, 331), from the oriental sarsaparilla of *Hemidesmus indicus*]. These crystals have but little odour, a biting taste, producing nausea and even giddiness, and a slight acid reaction. They melt at 41°, and solidify on cooling, when touched with a glass rod. At 66°, they are converted into vapour, and volatilise completely below 100°. Their solution in oil of vitriol becomes blood-red when heated, pale red on addition of water. — They dissolve sparingly in cold, more freely in hot water, abundantly in alcohol, ether, and oils both fixed and volatile, and appear to form crystallisable compounds with the alkalis. — Landerer (*Repert.* 71, 329) also describes crystals different from the preceding, which separated at 2 or 3° from the aqueous extract of the root of *Smilax aspera.* They contained lime, were slightly acid, sparingly soluble in alcohol and ether, and were coloured blood-red by cold oil of vitriol, yellow on heating, and finally carbonised.

Preparation. 1. The root is exhausted with hot alcohol; $\frac{7}{8}$ of the alcohol distilled off from the tincture; the residue treated with animal charcoal; and the liquid filtered after 24 — 78 hours, whereupon the pariglin separates in the form of a granular powder, which may be purified by recrystallisation from alcohol (Thubeuf, Poggiale). 10 lbs. of the roots yield about 3 oz. of pariglin (Thubeuf). — 2. The extract of the root prepared with boiling water is mixed with sufficient milk of lime to give it an alkaline reaction; the precipitate is collected on a linen cloth, decomposed by carbonic acid, and boiled, after drying and pulverising, with spirit of 40° B.; and the tinctures are evaporated till they deposit pariglin on standing (Pallotta). Batka treats the extract of the root prepared with absolute alcohol, with boiling water, which takes up the pariglin; evaporates to dryness; treats the residue with hydrochloric acid; then washes and dries the flocks which remain undissolved. — 3. A simpler process is to precipitate the concentrated decoction of the root with hydrochloric acid; dissolve the washed precipitate in sulphuric acid; precipitate with ammonia; and, if necessary, purify the precipitate by repeated solution in alcohol and treatment with animal charcoal (Poggiale). — 4. The comminuted root is exhausted with boiling alcohol; the tincture is precipitated by water; the precipitate washed with ether, and dissolved in alcohol; and the liquid evaporated after decoloration by animal charcoal (Lamatsch, *N. Repert. Pharm.* 6, 229). The alcoholic extract may also be dissolved in water, and absolute alcohol added to the solution; the pariglin is then precipitated, together with other substances, and may be extracted by boiling alcohol. Or the aqueous extract is exhausted with alcohol of 75 p. c., the tincture evaporated, and the residue treated with water, which leaves the pariglin undissolved.

Properties. Pariglin (hydrated, according to Poggiale, vid. inf.) crystallises in white needles made up of radiating laminæ (Thubeuf). It is usually obtained as a light powder permanent in the air (Pallotta), from alcohol in slender needles (Poggiale). Melts below 125° (Pallotta). Heavier than water (Poggiale). Has a peculiar odour (Pallotta), no odour (Thubeuf, Poggiale). Tastes bitter and sharp, slightly astringent and nauseating (Pallotta); in the dry state it is nearly tasteless, in solution it tastes sharp and bitter (Thubeuf), strong and nauseating (Poggiale). In aqueous or alcoholic solution it reddens turmeric slightly (Pallotta, Poggiale), turns violet-juice green, but has no action on litmus (Poggiale). Petersen found pariglin, even in solution, tasteless and·neutral to turmeric. Batka's pariglin has an acid reaction, arising, according to Poggiale, from adhering hydrochloric acid. Béral (*J. Chim. méd.* 15, 134) regards pariglin as volatile.

Calculations.

	a.				b.		
42 C	....	252	....	63·31	32 C	192	.... 60·38
34 H	... ...	34	.. ..	8·54	30 H........	30	.... 9·43
14 O	....	112	....	28·15	12 O	96	.... 30·19

$C^{42}H^{34}O^{14}$.... 398 .... 100·00 $\qquad$ $C^{32}H^{30}O^{12}$.. 318 .... 100·00

30 C	....	180	.... 62·94
26 H	....	26	.... 9·09
10 O	....	80	.... 27·97

$C^{30}H^{26}O^{10}$ .... 286 .... 100·00

Analyses.

	O. Henry. at 100°.	Petersen. at 100°; mean.	Poggiale. at 120°.
C	62·84	............,... 62·79	.... 60·93 to 62·09
H................	9·76	.... 9·37	.... 8·28 ,, 8·96
O	27·40	.... 27·84	
	100·00	.... 100·00	

Free from nitrogen (Thubeuf). O. Henry found in purer pariglin 8·7 p. c. hydrogen. — *a,* according to Delffs's (*N. Jahrb. Pharm.* 11, 360) ; Poggiale gives the formula $C^8H^{7\cdot5}O^3$; Petersen (*Ann. Pharm.* 17, 166) the formula $C^{16}H^{13}O^5$: these formulæ, multiplied by 4 and by 2 respectively, yield the formulæ *b* and *c.* — According to Walz (*N. Jahrb. Pharm.* 12, 155), Delffs and O. Gmelin (*Ann. Pharm.* 110, 174), pariglin belongs to the glucosides, a view which is not reconcilable with the statements of Poggiale.

Decompositions. 1. Pariglin *heated* in a glass tube, melts, gives off a pungent odour like that of burnt bread, and then an odour of resin (Thubeuf). — 2. On red-hot coals, it takes fire and *burns away* without residue. — 3. Heated with *sulphur,* it melts and decomposes, giving off sulphurous and hydrosulphuric acids and forming sulphuric acid (Poggiale). — 3. *Chlorine gas* at ordinary temperatures colours it yellow, and converts it, at the melting point of pariglin, into a soft yellow substance, which becomes indistinctly crystalline on cooling (Poggiale). — 4. Its aqueous solution forms a saffron-coloured liquid with *iodine* (Thubeuf). — 5. It dissolves in strong *nitric acid,* the solution when heated giving off a large quantity of nitrous gas, and leaving when evaporated a brittle residue, which dissolves completely

in boiling water, settles down in white flocks on cooling, and does not crystallise from alcohol (Thubeuf). When pariglin is dissolved in cold strong nitric acid, part of it turns yellow and decomposes, but the precipitate thrown down from the solution by water consists almost wholly of undecomposed pariglin (Poggiale). — In this reaction (or according to Batka, when the solution is evaporated with nitric acid), neither oxalic acid (Poggiale), nor mucic acid is produced, and the pariglin remains undecomposed (Batka).

6. When *oil of vitriol* is dropped upon pariglin, the pariglin assumes a dark red, then a violet, and lastly a pale yellow colour, dissolves, and is precipitated from the solution by water in its original state (Poggiale). The red solution in oil of vitriol becomes purple-red on addition of a drop of water (Batka), violet-red when gently heated (Thubeuf). — Pariglin dissolves in *hydrochloric acid*, the solution assuming the colour of wine-lees, when gently heated, and solidifying to a jelly (Thubeuf, Walz). According to Batka pariglin is precipitated by hydrochloric acid from its aqueous solution. According to Poggiale, the solution of pariglin in hydrochloric acid yields by evaporation, well developed crystals; pariglin dissolves better in acidulated than in pure water, and is precipitated from the solutions by alkalis. The dilute hydrochloric acid solution leaves on evaporation small scales; the sulphuric acid solution leaves prisms of otherwise unaltered pariglin (Poggiale). According to Palotta, pariglin forms salts with acids.

Combinations. — *With water.* Crystallised pariglin loses in drying, 8·56 p.c. water.

Pariglin dissolves in cold, and more abundantly in hot water, separating out as the solution cools (Thubeuf). The solution froths when shaken (Batka).

It dissolves in aqueous *ammonia, potash* and *soda* (Poggiale). With ammonia it forms an emulsion, which becomes clear and frothy as the excess of ammonia evaporates, and leaves a frothy mass when completely evaporated. The latter forms with water an opalescent solution, which becomes turbid on addition of a drop of absolute alcohol, and has an acid reaction (Batka). — It is precipitated from its aqueous solution by *chloride of calcium*; from the alcoholic solution by alcoholic *neutral acetate of lead* (Batka). — It does not combine with *magnesia*,

Pariglin dissolves very slightly in cold, very easily in boiling *alcohol*, forming a frothy liquid (Pallotta, Poggiale). It is more soluble in hydrated than in absolute alcohol (Thubeuf, Batka). — According to Poggiale, it dissolves in boiling ether: according to Thubeuf and Lamatsch, neither in cold nor in boiling ether, but easily according to Thubeuf in hot *ether-alcohol.* — It dissolves in *volatile*, less easily in *fixed oils* (Poggiale).

5. Xylosteïn.

HUEBSCHMANN. *Verhandl. des Schweizer Apothekervereins* (1845), abstr. *Pharm. Viertelj.* 5, 197.

J. B. ENZ. *Pharm. Viertelj.* 5, 196; abstr. *Chem. Centr.* 1856, 193.

The bitter principle of the berries of the fly honeysuckle (*Lonicera Xylosteum*).

Preparation. 1. The berries are exhausted with alcohol; the tincture is digested with milk of lime; the alcohol is distilled off from the filtrate; the residue is treated with ether, which takes up the xylosteïn; the solution is evaporated to dryness; and the residue is dissolved in boiling water and treated with animal charcoal; xylosteïn then crystallises from the filtrate. — 2. The crushed berries are boiled with a sufficient quantity of water; the decoction is precipitated by neutral acetate of lead; the lead is removed from the filtrate by hydrosulphuric acid; and the liquid, again filtered, is evaporated to a syrup. This syrup repeatedly shaken up with ether yields xylosteïn which crystallises out by spontaneous evaporation and may be rinsed with cold water (Enz).

Properties. Colourless, very long needles or prisms. Inodorous. Slightly bitter. Melts at 100° to colourless drops which solidify in the crystalline form on cooling. Neutral. Free from nitrogen (Hübschmann, Enz).

Decompositions. When *heated* it gives off heavy white fumes, forms a crystalline sublimate, and leaves charcoal (Hübschmann). — *Oil of vitriol* colours it brown. — It is not attacked by *dilute acids* in the cold, but when heated it is resolved into sugar and other products (Enz).

Combinations. Sparingly soluble in cold, easily in boiling *water*, whence it crystallises on cooling. — The (aqueous?) solution exhibits a white turbidity when mixed with *basic acetate of lead* (Enz). It dissolves very easily in *alcohol* and *ether* (Hübschmann).

COMPOUNDS CONTAINING 26 AT. CARBON.

Primary Nucleus $C^{26}H^{14}$; *Oxyazo-nucleus* $C^{26}N^2H^{10}O^2$.

Harmine.

$$C^{26}N^2H^{12}O^2 = C^{26}N^2H^{10}O^2,H^2.$$
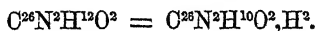
FRITZSCHE. (Harmine, Harmaline, and their derivatives). 1. *Petersburg. Acad. Bull.* 6, 49; *J. pr. Chem.* 41, 31; and 42, 275; *Pharm. Centr.* 1847, 449; *Ann. Pharm.* 64, 360; *N. J. Pharm.* 13, 373; *Lieb. Kopp. Jahresb.* 1847-8, 636. — 2. *Petersb. Acad. Bull.* 6, 242; *Pharm. Centr.* 1847, 769; *Lieb. Kopp. Jahresb.* 1847-8, 639. — 3. *Petersb. Acad. Bull.* 6, 289; *J. pr. Chem.* 43, 144; *Pharm. Centr.* 1848, 49; *Ann. Pharm.* 68, 351; *N. J. Pharm.* 14, 73; *Lieb. Kopp. Jahresb.* 1847-8, 641. — 4. *Petersb. Acad. Bull.* 7, 129; *J. pr. Chem.* 44, 370; *Ann. Pharm.* 68,

355; *Pharm. Centr.* 1848, 561. — 5. *Petersb. Acad. Bull.* 8, 81; *J. pr. Chem.* 48, 175; *Ann. Pharm.* 72, 306; *Pharm. Centr.* 1849, 833; *Lieb. Kopp. Jahresb.* 1849, 386. — 6. *Petersb. Acad. Bull.* 12, 17; *J. pr. Chem.* 60, 359; *Ann. Pharm.* 88, 327; *Pharm. Centr.* 1853, 937; *Lieb. Kopp. Jahresb.* 1853, 478. — 7. *Petersb. Acad. Bull.* 12, 33; *J. pr. Chem.* 60, 414; *Ann. Pharm.* 88, 328; *Pharm. Centr.* 1854, 2; *Chem. Gaz.* 1854, 161; *Lieb. Kopp. Jahresb.* 1853, 478. — 8. *Petersb. Acad. Bull.* 12, 225; *Ann. Pharm.* 92, 330; *Pharm. Centr.* 1854, 340; *Chem. Gaz.* 1854, 472; *Lieb. Kopp. Jahresb.* 1854, 526.

The papers cited under 1, 2, 6, 7 and 8, contain the matter relating to harmine.

Leucoharmine.

Occurrence. In the seeds of *Peganum Harmala*, to the amount of about $1\frac{1}{3}$ per cent.

Formation. By the action of moderately warmed nitric acid on harmaline, or by heating harmaline with bichromate of potash.

Preparation. A. *From the seed of Peganum Harmala.* The pulverised seeds are exhausted in a displacement apparatus with cold water containing acetic or sulphuric acid; any excess of acid that may be present in the extract is neutralised; and a considerable quantity of solution of common salt is added, which throws down both harmine and harmaline as hydrochlorates. These are washed with solution of common salt, then dissolved in cold water, which leaves colouring matter undissolved; the solution is decolorised with animal charcoal; and ammonia is added by drops to the filtrate, heated to 50° or 60° and well stirred, till a precipitate begins to form. This precipitate, which increases rapidly on continuing the stirring, without any further addition of ammonia, usually contains all the harmine, without any admixture of harmaline. Its purity may be tested by the microscope, which exhibits the harmine in needles, the harmaline in laminæ. Or the hot solution in acidulated alcohol is mixed with excess of ammonia, which quickly throws down the harmine in needles, whereas the harmaline separates gradually and after some time only. The precipitate produced by ammonia is collected, and any harmine that may remain in the filtrate is precipitated by cautious addition of ammonia. If the original precipitate contains harmaline, it must be purified by dissolving the whole of it in acid, and partially precipitating the solution in the manner above described. The whole of the harmine thus obtained is purified by recrystallisation and decolorisation with animal charcoal.

B. *From Harmaline.* 1. Nitrate of harmaline is heated with a mixture of hydrochloric acid and alcohol in equal parts, till the liquid begins to boil from formation of an ether. The vessel is then removed from the fire; the liquid cooled till the hydrochlorate of harmine which has been formed separates out; this salt is collected, washed with dilute hydrochloric acid, and dissolved in cold water; and the harmine is precipitated by potash or ammonia. It may be purified by solution in water acidulated with sulphuric acid, and decoloration with animal charcoal, or by precipitating the acid solution with hydrochloric acid, common salt, nitric acid, or nitrate of soda, either of which throws down the harmine in the form of a salt. From the hot aqueous solution of this salt, the harmine is precipitated by dilute

aqueous ammonia in very slender crystals; larger crystals are obtained by dissolving it in the smallest possible quantity of acetic acid, slowly heating the solution, and collecting the crystals before the liquid cools. — 2. When bichromate of harmaline is heated to above 120° in a capacious flask from which the air is excluded, decomposition takes place, attended with evolution of heat, and part of the harmine thereby produced volatilises and collects on the sides of the flask. The product is dissolved in boiling alcohol, or in warm water acidulated with hydrochloric acid, a dark-coloured secondary product then remaining behind, and the solution is treated as above described (B. 1). By this process only one-fourth of the bichromate of harmaline used is converted into harmine.

Properties. Colourless, very brittle crystals, having a strong lustre and high refracting power (Fritzsche). Rhombic prisms, with angles of 124° 18' and 55° 42' (Nordenskjoeld, *Petersb. Acad. Bull.* 6, 242). Oblique rhombic prisms *u (fig. 96)* having the basal end-face *l* and the front oblique end-face *i (fig. 95)* set upon the acute lateral edges (they are obtuse in the figure) ; the edges between *l* and *u* behind truncated by the octahedral faces *h*. angle *u : u* in front $= 53°\ 48'$; $u : l = 97° 32'$; $l : i = 165° 32'$ (calc. 165° 34'); $i : u = 103° 35'$ calc.; $h : h = 118° 0'$ calc.; $h : l = 145° 5'$; $h : p = 117° 23'$. The character of the crystals is prismatic, sometimes *i* sometimes *l* predominating at the ends. The prisms are about 10 mm. long, only $\frac{1}{2}$ mm. thick, often hollow, and have an adamantine lustre (Schabus).

Tasteless in the solid state, bitter in solution. Permanent in the air both in the solid state and in solution.

					Fritzsche.		
				a	*b.*		*c.*
26 C	....	156	....	73·58	.... 73·51	.... 73·70	.... 74·13
2 N	....	28	....	13·21	....		13·02
12 H	....	12	....	5·67	.... 5·62	.... 5·64	.... 5·53
2 O	....	16	....	7·54			7·32
$C^{26}N^2H^{12}O^2$	....	212	....	100·00			100·00

a and *b* more recent; *c* mean of older analyses. Fritzsche originally gave for harmine, harmaline and their derivatives, formulæ containing 1 at. carbon more. Gerhardt (*Compt. Chim.* 1849, 346) suggested formulæ with 28 at. carbon.

By heating its *bichromate*, it is converted into a new base.

Nearly insoluble in *water*.

Harmine forms with *acids* colourless or faintly yellowish crystallisable *salts*, whose concentrated solutions have a yellowish colour, whereas the dilute (especially the alcoholic) solutions appear bluish by reflected light. The salts dissolve for the most part more abundantly in pure than in acidulated water, and are precipitated from their aqueous solutions by addition of hydrochloric acid, nitric acid, common salt, or nitrate of soda. From the solutions of the salts, potash and ammonia throw down harmine, part of which, however, remains dissolved. From the aqueous solution of ammonia-salts, harmine at the boiling heat expels the ammonia, but less easily than harmaline. — Bicarbonate of potash, and bihydrosulphate of ammonia, added to solutions of harmine-salts, also throw down the base in the free state, not in the form of a salt.

Sulphate of Harmine. — a. *Mono-acid.* — Dilute sulphuric acid is digested with excess of harmine; the filtrate is left to evaporate slowly, and the crystals which separate are recrystallised from boiling alcohol. — At 110° the salt gives up 6·57 p. c. water (2 at. = 6·45 p. c.) and then contains 15·14 p. c. sulphuric acid, corresponding with the formula $C^{26}N^2H^{12}O^2,HO,SO^3$ (calc. = 15·33 p. c. SO³). — It dissolves sparingly in cold, more easily in boiling water, without crystallising on cooling.

b. *Biacid.* — Separates on cooling from a solution of harmine in excess of boiling sulphuric acid mixed with alcohol, in anhydrous crystals very much like those of the mono-acid salt. Contains 25·59 p. c. sulphuric acid ($C^{25}N^2H^{12}O^2,2HO,2SO^3$ = 25·81 p. c. SO³).

Hydriodate and *Hydrobromate of Harmine*, obtained from the acetate by double decomposition, resemble the hydrochlorate.

Hydrochlorate of Harmine. The solution of harmine in water containing hydrochloric acid mixed with a large quantity of concentrated hydrochloric acid, deposits crystals, which must be washed with dilute hydrochloric acid. — Slender yellowish needles which give off 12·38 p. c. water at 100° (4 at. = 12·37 p. c.) and then contain a quantity of hydrochloric acid, answering to the formula $C^{26}N^2H^{12}O^2,HCl$ (calc. = 14·65 p. c. HCl). From its solution in strong alcohol it separates in colourless anhydrous crystals.

Nitrate of Harmine. — Precipitated by dilute nitric acid or by aqueous nitrate of ammonia from a solution of the acetate. Colourless needles, less soluble in water containing nitric acid than in pure water.

Chromate of Harmine. a. *Mono-acid.* From an aqueous solution of hydrochlorate of harmine, cold aqueous bichromate of potash throws down a light yellow powder, presenting under the microscope the aspect of small spherules; it quickly decomposes into harmine and bichromate of harmine.

b. *Bi-acid.* — On mixing acid solutions of harmine with aqueous chromic acid or alkaline chromates, drops of oily liquid separate, which soon solidify in the crystalline form. When a solution of harmine in excess of acetic acid is dropped into a boiling aqueous solution of chromic acid mixed with acetic acid, beautiful crystals are obtained. — Slender yellow needles, sparingly soluble in cold, somewhat more soluble in boiling water. Dissolves without decomposition in boiling alcohol. For the decomposition by *heat*, see page 105.

				Fritzsche. *mean.*
26 C	156	....	48·00	.... 48·82
2 N	28	....	8·62	
13 H	13	....	4·00	.... 3·85
3 O	24	....	7·38	
2 CrO³	104	....	32·00	.... 30·96
$C^{26}N^2H^{12}O^2,HO,2CrO^3$	325	....	100·00	

Chloromercurate of Harmine. — Mercuric chloride added to a cold

aqueous solution of hydrochlorate of harmine, throws down a curdy precipitate ; from a hot solution it throws down crystals.

Chloroplatinate of Harmine. — From a dilute solution of hydrochlorate of harmine, bichloride of platinum throws down flocks, which become crystalline when heated to 50°.

Fritzsche.

26	C	156·0	....	37·33	....	37·90
2	N	28·0	....	6·70		
13	H	13·0	....	3·12	....	3·17
2	O	16·0	....	3·82		
3	Cl	106·2	....	25·41		
	Pt	98·7	....	23·62	....	22·23

$C^{26}N^2H^{12}O^2,HCl,PtCl$ .... 417·9 .... 100·00

Harmine does not form a salt with *hydrocyanic acid.*

Hydrosulphocyanate of Harmine. — Dazzling white, slender interlaced needle-shaped crystals, precipitated by dilute aqueous sulphocyanide of potassium from hydrochlorate of harmine. Dissolves sparingly in cold, easily in boiling water, and separates on cooling.

Hydroferrocyanate of Harmine. — Precipitated by ferrocyanide of potassium from harmine-salts as a light yellow crystalline substance. Boiling solutions yield orange-yellow, anhydrous crystals, which when exposed to moist air, change their form and take up water, which they part with at the boiling heat.

Hydroferricyanate of Harmine. — Dirty yellow flocks precipitated by ferricyanide of potassium from cold solutions of harmine salts.

Acetate of Harmine. Harmine dissolves abundantly in cold acetic acid, the solution when heated depositing harmine, and leaving it almost free from acetic acid, when evaporated over the water-bath. If the solution be evaporated at mean temperature, free harmine is at first obtained, the acetate crystallising out only when the solution becomes concentrated to a syrup.

Oxalate. — a. *Diacid.* (*Neutral*).—Freshly precipitated harmine is added to a boiling solution of harmine in oxalic acid, until a crystalline precipitate, difficultly soluble in water, separates out.

b. *Mono-acid.* — The solution of harmine in excess of oxalic acid deposits fine tufts of needles, containing 5·67 p. c. water (2 at. = 5·62 p. c.). Difficultly soluble in cold *water.*

Fritzsche.
dried ; mean.

30	C	180	....	59·60	....	60·08
2	N	28	....	9·27		
14	H	14	....	4·64	....	4·58
10	O	80	....	26·49		

$C^{26}N^2H^{12}O^2,C^4H^2O^8$ .... 302 .... 100·00

Harmine dissolves with difficulty in cold, more easily in boiling *alcohol.* It is somewhat soluble in *ether,* slightly soluble in *rock-oil,* and more readily soluble in *oils of turpentine, of lemons* and *of olives.*

Oxychlorazo-nucleus C²⁶N²Cl²H⁸O².

Bichloroharmine.

$$C^{26}N^2Cl^2H^{10}O^2 = C^{26}N^2Cl^2H^8O^2,H^2.$$
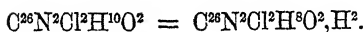
J. FRITZSCHE. *Petersb. Acad. Bull.* 5, 12; *Chem. Centr.* 1862, 209.

Formation and Preparation. — A very dilute solution (containing 1½ to 2 p. c.) of hydrochlorate of harmine is heated to boiling; 10 to 15 p. c. of strong hydrochloric acid is then added to it, and afterwards, the solution being still kept boiling, chlorate of potash is thrown in, by small quantities at a time, until the brownish red colour, which the liquid assumes at first, is changed to pure yellow. The ebullition is maintained a little while longer, so as to destroy a coloured product; the solution is then allowed to cool; the crystals of bichloroharmine which separate are washed with dilute hydrochloric acid, or with solution of chloride of sodium, and purified by crystallisation from alcohol, or re-solution in water and precipitation by hydrochloric or nitric acid. On redissolving the hydrochlorate of bichloroharmine in a large quantity of hot water, and boiling it for several hours with a great excess of soda-ley, crystals of bichloroharmine are deposited, which must be recrystallised from alcohol.

Properties.   Soft white needles.

						Fritzsche. *mean.*
26	C	156	...	55·53	...	55·65
2	N	28	...	9·97	...	10 50
2	Cl	71	...	25 25	...	25·66
10	H	10	...	3·56	...	3·67
2	O	16	...	5 69	...	4·52
C²⁶N²Cl²H¹⁰O²		281	...	100·00	...	100·00

Bichloroharmine forms a compound with *iodine*, corresponding to biniodide of nitroharmine (p. 112), and containing 46·45 p. c. iodine.

Insoluble in cold, very slightly soluble in boiling *water*.

With *acids* it forms crystallisable *salts*, which, like those of harmine, are very difficultly soluble in water containing acids or salts. The mono-acid (neutral) salts are decomposed to a certain extent, with separation of bichloroharmine, when a large quantity of water is poured upon them. Ammonia throws down bichloroharmine from their solutions, as an amorphous, colourless jelly; solution of soda acts in the same way, but in this case the precipitate becomes crystalline when long boiled with a great excess of soda solution. — Bichloroharmine displaces a trace of ammonia from a boiling solution of sal ammoniac; part of the dissolved bichloroharmine separates out on cooling, but the rest only on addition of ammonia to the filtrate.

Hydrochlorate of Bichloroharmine. — Obtained by dissolving bichloroharmine in water containing hydrochloric acid, and precipitating by excess of hydrochloric acid. Crystallises from water in needles, from

alcohol in larger crystals; chloride of sodium separates it from its solutions in the form of a jelly which turns to needle-shaped crystals Contains 4 at. water, which it gives off at 100°, but reabsorbs 2 at if exposed to moist air. When heated much above 100°, it becomes yellow and loses hydrochloric acid; melts between 180° and 200° to a brown yellow liquid which dissolves in water and contains a newly formed base.

Nitrate. — Precipitated as a jelly, which afterwards changes to crystalline needles, by addition of excess of nitric acid to a solution of bichloroharmine in water containing nitric acid. Anhydrous and less soluble in water than the hydrochlorate. When melted it gives off acid vapours and yields a brown mass, from the solution of which in aqueous alkalis acids throw down brown flocks.

Nitrate of bichloroharmine precipitates from *oxide of argentam-monium* a pale-greenish jelly, containing silver. — When hydro-chlorate of bichloroharmine is mixed with nitrate of silver, a jelly is precipitated, without formation of chloride of silver, but, on adding nitric acid to the jelly, chloride of silver is formed.

Bichloroharmine dissolves in *alcohol, ether, benzene,* and *sulphide of carbon,* much more easily when heated than it does in the cold.

Oxynitroazo-nucleus $C^{26}N^2XH^9O^2$.

Nitroharmine.

$$C^{26}N^3H^{11}O^6 = C^{26}N^2XH^9O^2,H^2.$$
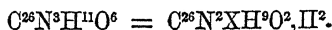
FRITZSCHE. See references 7 and 8 under Harmine.

Nitroharmidine. — Produced by the action of hot concentrated nitric acid on harmaline or on nitroharmaline.

Preparation. One part of harmaline is dissolved in 2 pts. water and the necessary quantity of acetic acid, and the solution is allowed to flow in a fine stream into 12 pts. boiling nitric acid of spec. grav. 1·4; a violent evolution of red fumes ensues, after which the ebullition is still continued for a short time ; the liquid is then cooled by addition of ice, or by being placed in cold water, and is mixed with excess of potash-ley, which precipitates nitroharmine, but retains in solution a resin, formed at the same time, which gives it a red-brown colour. The nitroharmine is dissolved in hot water containing hydrochloric acid ; the solution is filtered hot and mixed with concentrated hydrochloric acid ; the hydrochlorate, which separates on allowing the liquid to stand for a considerable time, is collected, washed with dilute hydrochloric acid, dissolved in boiling water, and the solution is decomposed by ammonia. The nitroharmine thus precipitated is recrystallised from hot alcohol. If less nitric acid is employed than the quantity prescribed above, more resin is formed. It is also necessary to avoid using nitric acid containing hydrochloric acid, and not to add the acid gradually to the solution of harmaline, since in the first case chloronitroharmine is produced, and in the second, a large quantity of resin.

Properties. Fine, sulphur-yellow needles, of a silky lustre, or small, dark yellow quadratic octahedra and quadratic tables. Crystals of the latter form are obtained by rapid cooling of alcoholic solutions; they quickly turn to needles when left in the solution. — Tasteless.

<div align="right">Fritzsche.</div>

26 C	....	156	. ...	60·70	....	60·73	
3 N	....	42	....	16·34	....	16·00	
11 H	. ...	11	. ..	4·28	.. ..	4·23	
6 O	. ....	48	.	18·68	.. . ...	19·04	

$$C^{26}N^2XH^{11}O^2 \;.. \; 257 \quad ..... . \; 100·00 \quad ..... . \; 100·00$$

Decompositions. 1. *Iodine* converts alcoholic nitroharmine into biniodide of nitroharmine. — 2. *Bromine* and *chlorine* form bromo- and chloronitroharmine by acting on aqueous salts of nitroharmine; when the action is continued longer, they give rise to resinous products. — 3. On heating bichromate of nitroharmine, a new base, different from nitroharmine, is formed.

Combinations. Nitroharmine dissolves slightly in cold *water*, more abundantly in hot water, and separates again partially on cooling.

It forms with *acids*, crystallisable, bright yellow *salts*, which have a slight bitter taste. They are precipitated from their aqueous solutions, like the salts of harmine, by acids and salts.— Nitroharmine gradually displaces a small quantity of ammonia from a boiling solution of sal-ammoniac.

Sulphate of Nitroharmine. — a. *Mono-acid.* — Freshly precipitated nitro-harmine is stirred up with warm water; sulphuric acid is added in quantity not sufficient for complete solution; and the mixture is filtered and allowed to cool, when bright yellow needles of the monoacid salt are deposited. — b. *Bi-acid.* — The solution of the mono-acid salt mixed with a large quantity of oil of vitriol deposits the bi-acid salt, in yellow needles as it cools.

Hydriodate. — Precipitated by iodide of potassium from a solution of acetate of nitroharmine. Sometimes a brown jelly separates at the same time; doubtless an iodine-compound of nitro-harmine.

Hydrochlorate. — A solution of nitroharmine in acetic acid or in warm water containing hydrochloric acid, is mixed with excess of concentrated hydrochloric acid, whereupon slender needles are quickly deposited, and the solution, if strong, solidifies to a magma of crystals. The salt is washed with dilute hydrochloric acid, pressed between blotting paper, dissolved in boiling alcohol, the solution digested upon animal charcoal, filtered and left to cool. — Pale yellow needles, which contain 4 at. water when dried over oil of vitriol. — Soluble in water and alcohol, dissolves with difficulty in water containing hydrochloric acid.

	Over oil of vitriol.				Fritzsche.
C²⁶N²XH¹¹O²	....	257	....	78·02	
HCl	....	36·4	....	11·05	.... 10·78
4HO	....	36	....	10·93	

$$C^{26}N^2XH^{11}O^2,HCl + 4HO. \; 329.4 \; ,....... \; 100·00$$

Nitrate. a. *Basic.* — When freshly precipitated nitroharmine is suspended in water, and a quantity of nitric acid is added, less than sufficient to dissolve it, then dilute ammonia until turbidity commences, the filtered liquid deposits a small quantity of a deep-yellow precipitate, and a further quantity on addition of ammonia. Under the microscope, this precipitate appears to be composed of fibres much crumpled and twisted. It contains nitric acid, and is probably basic nitrate of nitroharmine. It is slightly soluble in cold water, partially soluble in boiling water, with separation of needles. Ammonia and solution of potash do not act upon it in the cold; when heated with the latter it changes to needles; soluble in hot alcohol, and separates in part unchanged on cooling.

b. *Mono-acid.* — Precipitated by nitric acid, from solutions of the salts of nitroharmine, in bright yellow needles, which, when left in the liquid, change to dark yellow granules. — Slightly soluble in pure water; still less so in presence of nitric acid.

Chromate. — Crystalline precipitate thrown down by neutral or acid chromate of potash from solutions of the salts of nitroharmine.

Chloromercurate. — Mercuric chloride throws down a flocculent jelly from cold aqueous hydrochlorate of nitroharmine; from hot dilute solutions it throws down microscopic bundles of crystals.

Nitroharmine and Silver-oxide. — The perfectly neutral solution of nitrate of nitroharmine is mixed with ammonio-nitrate of silver. The product is a dark, orange-red, transparent jelly, which dries up to brownish red amorphous lumps.

Chloroplatinate. — When bichloride of platinum is dropped into a dilute boiling solution of hydrochlorate of nitroharmine, needles or foliated prisms separate out, which are difficultly soluble in cold or boiling water.

Hydroferrocyanate. — Ferrocyanide of potassium precipitates from cold concentrated solutions of nitroharmine salts, a jelly; from boiling or acid, very dilute solutions, brown microscopic crystals, which are very slightly soluble in water.

Hydroferridcyanate. — Obtained like the previous salt with ferridcyanide of potassium. More soluble in boiling water than the last salt, and separates in yellow granules on cooling.

Cyanide of Mercury and Nitroharmine. — Yellow prisms, which separate on cooling from solutions of acetate of nitroharmine and mercuric cyanide, mixed boiling hot.

Hydrosulphocyanate. — Very small, almost colourless needles, precipitated by sulphocyanide of potassium from solutions of nitroharmine salts.

Acetate. — A boiling, saturated solution of nitroharmine in concentrated acetic acid and alcohol, gradually deposits yellow, well-formed, transparent crystals. They become opaque when washed with water, and are completely decomposed, by boiling with water, into nitroharmine and acetic acid.

Nitroharmine is soluble in cold, still more so in boiling, *alcohol*. It dissolves slightly in *ether*, easily in boiling *coal-tar naphtha* and boiling *rock-oil*, crystallising out almost completely on cooling.

Biniodide of Nitroharmine.

$$C^{26}N^2XH^{11}O^2,I^2.$$
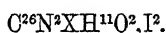
FRITZSCHE. See references 7 and 8, page 104.

Biniodide of Nitroharmidine, Iodonitroharmidine.

Solution of iodine in coal-tar naptha is added to a solution of nitroharmine in the same liquid, until a purple-red colour indicates the presence of excess of iodine; the precipitate, which forms immediately, is filtered off, and washed with coal-tar naphtha.

A loose mass of yellowish brown, microscopic needles, unalterable at 100°.

	Air-dried.			Fritzsche. *mean.*
$C^{26}N^2XH^{11}O^2$........	257	....	50·49	.... 51·3
2I	252	....	49·51	.... 48·7
$C^{26}N^2XH^{11}O^2,I^2$ ...	509	....	100·00	.... 100 0

It may also be regarded as nitroharmaline in which H^2 is replaced by I^2; but the modes of formation and decomposition are against this view.

Decompositions. When boiled with dilute *sulphuric acid*, it splits up into iodine and nitroharmine; when boiled with *ammonia, sulphide of ammonium, potash-ley*, or *alcohol*, it is decomposed, with separation of nitroharmine. — It dissolves in considerable quantity in concentrated *hydrocyanic acid* at ordinary temperatures, giving a pale yellow solution, which deposits a red-brown crystalline mass when evaporated. The solution in hot hydrocyanic acid deposits, on cooling, larger ruby-red prisms, containing less iodine than biniodide of nitroharmine and differing from this body.

Combinations. — Almost completely insoluble in cold, and very slightly soluble in boiling *water*.

It appears to behave towards *hydrochloric acid* as a base. When that acid is poured over it, it turns black, and becomes covered with dark, still smaller microscopic needles; when it is evaporated with hydrochloric acid, iodine volatilises, and there remains hardly anything but hydrochlorate of nitroharmine. Biniodide of nitroharmine dissolves in alcoholic hydrochloric acid, giving a yellow solution which nearly solidifies on cooling, from the separation of exceedingly fine needles.

Biniodide of nitroharmine dissolves abundantly in boiling glacial *acetic acid;* the brown solution deposits dark-coloured crystals on cooling. Almost insoluble in cold *alcohol, ether,* and *coal-tar naphtha;* very slightly soluble on boiling.

Oxybromonitroazo-nucleus $C^{26}N^2XBrH^8O^2$.

Bromonitroharmine.

$$C^{26}N^3BrH^{10}O^6 = C^{26}N^2XBrH^8O^2,H^2.$$
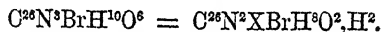
FRITZSCHE.   See reference 8, page 104.

Bromonitroharmidine.

When dilute bromine-water is added to a very dilute solution of a salt of nitroharmine, the smell of bromine disappears immediately, and on addition of ammonia, bromonitroharmine is precipitated, and may be purified by recrystallisation from alcohol.

Resembles chloronitroharmine (see below). Forms salts with acids, and unites with iodine and bromine.

Bibromide of Bromonitroharmine.

$$C^{26}N^2XBrH^{10}O^2,Br^2.$$
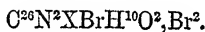
FRITZSCHE.   See reference 8, page 104.

Bibromide of Bromonitroharmidine.

Bromine-water, added in moderate excess to a solution of bromo-nitroharmine in weak alcohol, causes a milky turbidity, which disappears by a gentle heat.   The compound separates on cooling and stirring, in yellow, microscopic needles.

Oxychlornitroazo-nucleus $C^{26}N^2XClH^8O^2$.

Chloronitroharmine.

$$C^{26}N^3ClH^{10}O^6 = C^{26}N^2XClH^8O^2,H^2.$$
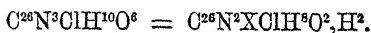
FRITZSCHE.   See reference 8, page 104.

Chloronitroharmidine. — Formed by the action of chlorine on nitro-harmine, or of nitrohydrochloric acid on harmaline.

. *Preparation.* 1. Chlorine-water is added to aqueous hydrochlorate or acetate of nitroharmine, as long as the smell of chlorine is destroyed; or chlorine gas is passed into the solution, whereupon chloronitro-harmine separates out in the form of a jelly.   The too long continued action of chlorine gives rise to a yellow resin.   The mixture is heated to boiling, and the resulting solution is precipitated by the cautious addition of ammonia, drop by drop, with constant stirring.   A more

or less crystalline product is thus obtained, whereas, from cold solutions, a jelly is precipitated, which is difficult to wash. — 2. A solution of 1 pt. harmaline in 2 pts. water and the requisite quantity of acetic acid is poured into 12 pts. of boiling nitric acid of sp. gr. 1·40, and 2 pts. of fuming hydrochloric acid are added to the mixture ; or the harmaline solution is poured into the boiling mixture of the two acids. The liquid becomes red-brown, froths up strongly, and evolves a volatile substance which attacks the eyes, but deposits nothing but resin on cooling. In order to separate the dissolved chloronitroharmine, a solution of sal-ammoniac, cooled by placing lumps of ice in it, is poured into the liquid ; this is diluted with about an equal bulk of water ; and caustic soda is then added, until it smells strongly of ammonia, whereby an abundant precipitate of impure chloronitroharmine is thrown down. The product is washed with dilute hydrochloric acid and heated with water; the solution freed by filtration from undissolved resin, and precipitated by gradual addition of ammonia ; and the precipitate purified by crystallisation from hot alcohol. The crude chloronitroharmine may also be dissolved in boiling water, with addition of just the necessary quantity of nitric acid, and precipitated as nitrate from the cooled filtrate by addition of nitric acid in excess ; this salt, after being washed, may be dissolved in hot water, and pure chloronitroharmine precipitated from the boiling hot filtered solution by means of caustic ammonia.

Properties. Bright yellow, brittle mass, composed of very fine needles, which cannot be distinctly perceived, even under a magnifying power of 300. Ammonia precipitates it from cold solutions, as an almost transparent, deep yellow, very bulky jelly, which shrinks very much on drying. Tasteless; in solution slightly bitter and rough. Loses 11·44 per cent. water at 100° (4 at. = 10·98 per cent.), and becomes orange-yellow.

		at 100°.				Fritzsche.
26	C	156	....	53·54	....	54·51
3	N	42	....	14·40		
10	H	10	....	3·42	....	3·36
	Cl	35·4	....	12·18	....	12·07
6	O	48	....	16·46		
$C^{26}N^2XClH^{10}O^2$		291·4	....	100·00		

Decompositions. After drying at 100°, it leaves a reddish-yellow residue when alcohol or coal-tar naphtha is poured upon it, but dissolves completely when boiled with dilute nitric acid. — *Solution of iodine* converts it into biniodide of chloronitroharmine (p. 115). When mixed with solution of iodide of potassium, and then with nitric acid, it deposits a deep blue precipitate.

Combinations. Dissolves but slightly in cold *water ;* more abundantly in boiling water, giving a yellow solution.
It forms pale yellow *salts* with *acids.* When boiled with solution of sal-ammoniac, it only slowly displaces a trace of ammonia.

Sulphate of Chloronitroharmine. — a. *Mono-acid.* —When chloronitroharmine is dissolved in warm alcohol containing sulphuric acid, this

salt separates on cooling in globular groups of capillary needles. It is obtained in bright yellow, gelatinous flocks by cooling the hot aqueous solution.

b. Bi-acid. — The concentrated, hot, alcoholic solution of harmine mixed with excess of sulphuric acid, gradually yields needles of the acid salt on cooling.

Hydrochlorate. — Chloronitroharmine is dissolved in hot alcohol mixed with excess of hydrochloric acid. — Fine capillary crystals moderately soluble in water. Precipitated from its aqueous solution by a large excess of hydrochloric acid, as a yellow jelly; by chloride of sodium in white flocks.

Nitrate. — Stellate groups of fine needles.

Chloronitroharmine with Oxide of Silver. — Precipitated by ammonio-nitrate of silver from a perfectly neutral solution of nitrate of chloronitroharmine.

Chloroplatinate. — Hot alcoholic solutions of hydrochlorate of chloro-nitroharmine and bichloride of platinum deposit this salt, on cooling, in fine yellow prisms.

					Fritzsche.
26	C	156	31·40		32·07
3	N	42	8·44		
11	H	11	2·21		2·27
6	O	48	9·64		
4	Cl	141·6	28·50		
	Pt	98·7	19·81		19·58

$C^{26}N^2XClH^{10}O^2,HCl,PtCl^2$.. 497·3 .... 100·00

Chloronitroharmine is moderately soluble in boiling *alcohol*, but slightly soluble in *ether*. It dissolves abundantly in boiling *coal-tar naphtha* and in *rock-oil*.

Biniodide of Chloronitroharmine.

$$C^{26}N^2XClH^{10}O^2,I^2.$$

FRITZSCHE. See reference 8, page 104.

Biniodide of Chloronitroharmidine.

Separates in fine needles, resembling biniodide of nitroharmine, from a mixture of the hot solutions of iodine and chloronitroharmine in alcohol or in coal-tar naphtha. — More soluble in alcohol than biniodide of nitroharmine; dissolves easily in warm alcoholic hydro-cyanic acid, and separates on cooling in brown, rounded granules.

			Fritzsche.
$C^{26}N^2XClH^{10}O^2$ .... 291·4	.... 53·62	.... 53·48
2I 252	.... 46·38	.... 46·52

$C^{26}N^2XClH^{10}O^2,I^2$ .... 543·4 .... 100·00 .... 100·00

Primary Nucleus $C^{26}H^{16}$; *Oxyazo-nucleus* $C^{26}N^2H^{12}O^2$.

Harmaline.

$$C^{26}N^2H^{14}O^2 = C^{26}N^2H^{12}O^2,H^2.$$
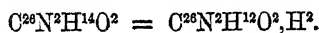
Göbel (1841). *Ann. Pharm.* 38, 3C3.
Varrentrapp & Will. *Ann. Pharm.* 39, 289.
Fritzsche. See references on page 104.

The preparation of harmaline was first described by Gobel, after it had been already (*Bull. scient. Petersb.* 7, 291) mentioned by Fritzsche.

Occurrence. To the extent of 2 to 3 per cent. in the seeds of *Peganum Harmala;* almost exclusively in the husks, scarcely a trace in the grain.

Preparation. If in the preparation of harmine, as described at page 104, a small quantity of ammonia is added to the hydrochloric acid solution of harmine and harmaline, the former is precipitated and the latter remains in solution. The liquid is then mixed with excess of ammonia; the precipitate is suspended in water; acetic acid is added until nearly all is dissolved; the filtrate is precipitated with nitrate of soda, chloride of sodium, or hydrochloric acid; and the precipitated salt is washed with a dilute solution of the precipitant, and purified by treatment in aqueous solution with animal charcoal. The harmaline is precipitated from the solution by excess of potash-ley, and washed at first with water, finally with absolute alcohol; it is then dissolved in boiling absolute alcohol, and the solution is allowed to cool, completely protected from the air (Fritzsche). — Göbel exhausts the pounded seeds with boiling water acidulated with acetic acid; precipitates with potash; crystallises the product from absolute alcohol; redissolves it in acetic acid; decolorises the solution with animal charcoal; precipitates with potash or ammonia; and crystallises again from alcohol. The crystals thus obtained have still a yellowish brown colour.

Properties. Obtained from its alcoholic solution, if completely protected from air, in colourless crystals, belonging to the rhombic or right prismatic system, Fig. 71 without u, but with the longitudinal face m (*fig.* 73). $a: a$ (over y) $= 116°$ 34'; $a: a$ (behind) $= 131°$ 18'; $a: a$ (below) $= 83°$ 54'. (Nordenskiöld, *Petersb. Acad. Bull.* 6, 58.) By itself it has scarcely any taste; in solution it tastes purely bitter (Fritzsche); has a faint bitter taste, and is afterwards somewhat rough and sharp (Göbel). Does not lose weight at 190° (Varrentrapp & Will).

				Varrentrapp & Will.		Fritzsche. *mean.*		
				mean.		*earlier.*		*later.*
26 C	....	156	....	72·90	....	73·15	...	73·49	....	72·78
2 N	....	28	....	13·08	....	13·45	....	12·33		
14 H	....	14	....	6·54	....	6·76	...	6·59	....	6·48
2 O	....	16	..	7·48	..	8·64	....	7·59		
$C^{26}N^2H^{14}O^2$,		214	....	100·00	....	100·00	....	100·00		

Varrentrapp & Will analysed Gobel's harmaline : they gave the formula $C^{24}N^2H^{13}O$. Fritzsche's earlier formula contains 27 at. carbon.

Decompositions. 1. Harmaline *heated* in a platinum spoon melts to a brown-red liquid, evolves disagreeably smelling white vapours, takes fire, and leaves a combustible cinder. When heated in a small tube it yields a white, mealy sublimate (Göbel). — 2. Freshly precipitated or aqueous harmaline is coloured brown by exposure to *air*, especially air containing ammonia. (Fritzsche). For Göbel's statement see Harmala-red (p.119.) — 3. *Nitrate* of harmaline, warmed with alcoholic *hydrochloric acid*, is converted into harmine (p. 104): $C^{26}N^2H^{14}O^2 + O^2 = C^{26}N^2H^{12}O^2 + 2HO$. Harmaline, boiled with excess of *nitric acid*, yields first nitroharmaline ; then, by longer boiling, nitroharmine. — Boiling *nitrohydrochloric acid* yields chloronitroharmine. — 4. *Bichromate* of harmaline, heated above 120°, undergoes a decomposition which propagates itself through the whole mass, and produces harmine and a dark-coloured resin. — 5. With *hydrocyanic acid*, it forms hydro-cyanharmaline (Fritzsche).

Combinations. Harmaline is very slightly soluble in *water*.
It neutralises *acids* and forms with them easily soluble, crystalline *salts* (Göbel). These and their solutions are yellow (pure sulphur-yellow : Fritzsche), have a bitter taste, and are decomposed by ammonia or the fixed alkalis, with separation of harmaline (Göbel), although a larger quantity of the base remains dissolved than corresponds to its solubility in water (Fritzsche). From cold aqueous harmaline-salts, ammonia and potash precipitate oil-drops, which collect to resinous concretions in strong solutions, and quickly change to crystals in dilute solutions. In hot liquids, the oily-drops appear only for an instant. — With the aid of heat, harmaline displaces ammonia from its salts. — The salts of harmaline (like the corresponding harmine-salts) are more soluble in pure water than in water containing acids or salts, and are precipitated from their aqueous solutions by acids and salts (Fritzsche).

Carbonate of Harmaline. — The salts of harmaline yield with normal alkaline carbonates either no precipitate, or a precipitate of harmaline. — When concentrated solutions of bicarbonate of potash and acetate of harmaline are mixed together, bicarbonate of harmaline is thrown down, and can be obtained, without much decomposition, by washing with very cold water, and quickly pressing and drying in the air. — Fine needles, containing about 13 per cent. carbonic acid, and easily decomposed by water into harmaline and carbonic acid gas (Fritzsche).

Phosphate. — Exists, according to Göbel, in the seeds of *Peganum Harmala.* — The neutral salt is obtained in needle-shaped crystals by boiling excess of harmaline with dilute phosphoric acid and evaporating the filtrate. Phosphoric acid precipitates an acid salt from the aqueous solution of the neutral salt (Fritzsche).

Sulphite. — The solution of harmaline in aqueous sulphurous acid dries up to a yellow resin, without any traces of crystallisation (Fritzsche).

Sulphate. — a. *Mono-acid.* — A yellow resin, which changes to a

radiated crystalline mass over oil of vitriol, obtained by digesting dilute sulphuric acid upon excess of harmaline and evaporating the filtrate. — b. *Biacid.* — Precipitated in needles, which dissolve easily in water, by adding sulphuric acid to the solution of *a.* (Fritzsche).

Hydrosulphate. — By mixing concentrated solutions of bihydro-sulphate of ammonia and acetate of harmaline, fine prisms are obtained, which quickly decompose in the air after separation of the mother-liquor (Fritzsche).

Hydriodate. — Crystalline precipitate, difficultly soluble in water.

Hydrochlorate. — Aqueous acetate of harmaline is precipitated by excess of hydrochloric acid, and the precipitate is washed with dilute hydrochloric acid. If the salt has not a pure yellow colour, it is dissolved in water and precipitated by pouring the solution into dilute hydrochloric acid. — Long, slender, yellow needles, which lose 12·6 per cent. water when heated (4 at. = 12·57 per cent. water). — Dissolves easily in water and alcohol, especially with the aid of heat, slowly in hydrochloric acid or solution of common salt.

		at 125°.			Fritzsche. mean.
26 C	......	156	......	62·30	...... 63·12
2 N	......	28	......	11·18	
15 H	......	15	......	5·99	...... 5·83
2 O	......	16	......	6·39	
Cl	......	35·4	......	14·14	...... 13·74

$C^{26}N^2H^{14}O^2$,HCl. 250·4 ...... 100·00

Nitrate. — By precipitating acetate of harmaline with dilute nitric acid, or with nitrate of ammonia, needles are obtained which are sparingly soluble in pure water, and almost insoluble in water containing nitric acid (Fritzsche).

Chromate. a. *Mono-acid.* — On mixing together dilute solutions of acetate of harmaline and normal chromate of potash, harmaline is precipitated. Crystals of monochromate of harmaline are obtained by adding acetate of harmaline, drop by drop, to a cold, saturated, aqueous solution of mono-chromate of potash, as long as harmaline is separated, then filtering, and adding more acetate of harmaline to the filtrate. — The same compound separates as a semi-fluid, dirty yellow mass when crystals of mono-chromate of potash are thrown into a concentrated solution of acetate of harmaline. If the mass is rinsed with a little water, dissolved in a larger quantity, and the solution added to the mother-liquor, crystals of the salt separate out. — Bright yellow, flattened needles, sparingly soluble in water. Easily decomposed into harmaline and the biacid salt: on addition of acetic acid, this decomposition takes place immediately (Fritzsche).

b. *Biacid.* — Aqueous chromic acid, monochromate and bichromate of potash throw down, from dilute acid solutions of harmaline salts, orange-coloured drops, which soon harden to bunches of crystals. — Remains unchanged at 120°. For the decomposition at higher temperatures see page 117. Scarcely soluble in water, crystallises from its solution in boiling alcohol, but is decomposed by continued ebullition (Fritzsche).

Chloromercurate. — Separates in the form of fine needles when hot

solutions of mercuric chloride and hydrochlorate of harmaline are mixed together; from cold solutions it separates as a thick flocculent precipitate (Fritzsche).

Chloroplatinate. — Bright-yellow, light powder, composed of microscopic crystals.

						Fritzsche.
26 C	..	156	....	37·15	....	37·62
2 N	..	28		6·67		
15 H	..	15		3·57	....	3·56
2 O	..	16	....	3·82		
3 Cl	..	106·2	....	25·29		
Pt	..	98·7	....	23·50	....	23·28

$C^{26}N^2H^{14}O^2,HCl,PtCl^2$ 419·9 .... 100·00

Contains 24·52 per cent. platinum (Varrentrapp & Will).

Hydrosulphocyanate. — Obtained from sulphocyanide of potassium and hydrochlorate of harmaline. Bright yellow crystalline precipitate; after recrystallisation, slender flattened needles, with a silky lustre.

Hydroferrocyanate. — A dilute solution of hydrochlorate of harmaline is precipitated at boiling heat with ferrocyanide of potassium in excess. Vermilion-red crystalline powder and larger crystals. Quite insoluble in water (Fritzsche).

Hydroferridcyanate. — Separates from cold solutions in drops which change to dark greenish blue crystals. Insoluble in water (Fritzsche).

Acetate. — The solution of harmaline in acetic acid yields acetate of harmaline as an easily soluble crystalline salt by spontaneous evaporation; by evaporation at higher temperatures, harmaline separates (Fritzsche).

Oxalate. — If aqueous oxalic acid is boiled with harmaline in excess, needles of the diacid salt separate on cooling; from their solution, oxalic acid precipitates the mono-acid salt (Fritzsche).

Harmaline dissolves with difficulty in cold *alcohol*, easily on boiling. It is sparingly soluble in *ether*, and is precipitated by ether from the concentrated alcoholic solution as a crystalline powder. It is somewhat soluble in *rock oil*, *oil of turpentine*, and *oil of lemons*; the freshly distilled oils dissolve it without coloration if protected from the air. — Oil of turpentine, which has been exposed to the air, colours harmaline red on boiling; oil of lemons colours it dark brown. — Hydrochlorate of harmaline dyes cloth mordanted with alum a pale and fugitive yellow (Fritzsche). See also Harmala-red.

Appendix to Harmaline.

Harmala-red.

Göbel. *Ann. Pharm.* 38, 363.
Dollfuss & Schlumberger. *J. pr. Chem.* 30, 41.
Fritzsche. *Petersb. Acad. Bull.* 6, 300; *J. pr. Chem.* 40, 155; *Pharm. Centr.* 1848, 74.

Harmala, Porphyrharmin. — Harmala-seeds are used for obtaining a red dye. Göbel prepared the colouring matter, but did not describe his process. He regards harmala-red as a product of oxidation of harmaline; Fritzsche however disputes this.

When 1 pt. of powdered harmala-seeds is moistened with 2 pts. alcohol of 80 per cent., and allowed to stand for eight days or a fortnight in a closed vessel, the mixture acquires a dark-red colour, which becomes brighter and purer when the moistening with alcohol is repeated, and the smell of the latter at the same time disappears. The colouring matter thus formed can be precipitated, but not quite pure, from its acid solutions by alkalis. Beautiful purple-red, almost gelatinous flocks are thus obtained, which dry up to a dark, opaque mass, with a greenish iridescence, and are very slightly soluble in water. If dissolved in acid after drying, alkalis no longer precipitate it purple, but yellowish-red (Fritzsche).

Göbel's harmala-red is insoluble in water, moderately soluble in ether, and soluble in all proportions in absolute alcohol. With acids it forms red salts, and dyes wool or silk mordanted with sulphate of alumina from the lightest pink to the deepest poppy-red.

Conjugated Compounds of Harmaline.

Hydrocyanharmaline.

$$C^{26}N^3H^{15}O^2 = C^{26}N^2H^{14}O^2,HCy.$$
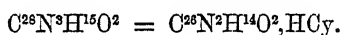
Fritzsche. See references 3 and 6, page 103.

Formation. By bringing together harmaline and hydrocyanic acid, or harmaline-salts and cyanide of potassium.

Preparation. 1. Harmaline is added to boiling dilute alcoholic hydrocyanic acid, as long as it is thereby dissolved; the solution is filtered hot, and on cooling hydrocyanharmaline crystallises out. — 2. A concentrated solution of acetate of harmaline is mixed with hydrocyanic acid, whereupon hydrocyanharmaline separates after some time, and may be freed from the mother-liquor by washing with water. Only a small product is thus obtained for the most part. — 3. An aqueous solution of a harmaline-salt is mixed with solution of cyanide of potassium, and the resulting amorphous precipitate, which would be decomposed by drying in the air, is dissolved while still moist in boiling alcohol, and allowed to crystallise by cooling. Cyanide of potassium gives an immediate crystalline precipitate with alcoholic harmaline-salts. Any harmaline that may remain mixed with it, can be removed by means of dilute acetic acid, which attacks hydrocyanharmaline comparatively little.

Properties. Colourless, thin, rhombic plates; permanent in the air and in vacuo.

Fritzsche.

28 C		168	....	69·71	....	69·81
3 N		42	....	17·43		
15 H		15	....	6·22	....	6·49
2 O		16	....	6·64	....	

$C^{26}N^2H^{14}O^2,HCy$ .... 241 .... 100·00

Decompositions. 1. Amorphous moist hydrocyanharmaline is partially decomposed, by drying in the air, into hydrocyanic acid and harmaline; crystallised hydrocyanharmaline does not undergo a similar partial decomposition till heated above 100° ; at about 180°, it is completely decomposed into the same products. — 2. It likewise splits up into hydrocyanic acid and harmaline when boiled with *water* or *alcohol.* — 3. When hydrocyanharmaline suspended in water is heated to boiling, with a great excess of *nitric acid*, the liquid assumes a beautiful purple-red colour, and deposits, when cold, a splendid red, amorphous powder, a further quantity of which can be obtained from the mother-liquor by addition of water, or by partial neutralisation with ammonia. The red powder is changed to a fine green by ammonia; alcohol dissolves it with beautiful purple colour, which, however, soon passes into a dirty yellow, but does not yield it again unaltered in evaporation. Ether is not coloured by it, but dissolves a part, probably a foreign admixture. — If hydrocyanharmaline is stirred up with water and poured into boiling nitric acid, a much smaller quantity of the red substance is formed. If alcohol is used instead of water, other products of decomposition are formed. — Hydrocyanharmaline heated with hydrochloric acid and *chlorate of potash* is converted into a resin.

Combinations. Hydrocyanharmaline is insoluble in *water.* — With *acids* it forms colourless *salts* of hydrocyanharmaline. These are partially decomposed, even by separation from their solutions, and more easily in proportion as the latter are more dilute. They are decomposed with peculiar facility when dried and kept. They cannot be prepared by acting on the corresponding harmaline-salts with hydrocyanic acid.

Sulphate of Hydrocyanharmaline. — Oil of vitriol dissolves hydrocyanharmaline without decomposition, forming a yellow liquid, which, by absorbing moisture from the air, or by careful dilution with water, is rendered colourless and deposits crystals of the sulphate. Moderately concentrated sulphuric acid converts hydrocyanharmaline into sulphate, without visibly changing its form or dissolving it. Hydrocyanharmaline dissolves in very dilute sulphuric acid to a clear, colourless liquid, which deposits part of the salt after a time in dense, microscopic crystals.

Hydrochlorate. — Crystals of hydrocyanharmaline, moistened with a small quantity of water or alcohol and then covered with hydrochloric acid, are converted into the hydrochlorate, without visible change of form, though under the microscope they are seen to be made up of an aggregation of small crystals. — Finely divided hydrocyanharmaline dissolves to a clear liquid in sufficiently dilute hydrochloric acid, whence a crystalline powder is generally deposited. This must be separated from the mother-liquor immediately, in order that it

may not be contaminated with hydrochlorate of harmaline, then washed with water, and dried as quickly as possible between filter-paper. — Colourless rhombic octahedrons. Splits up into hydrocyanic acid and hydrochlorate of harmaline when boiled with water.

				Fritzsche.
$C^{26}N^2H^{14}O^2$	214	....	77·14	.... 74·63
HCy....................	27	....	9·73	.... 9·51
HCl	36·4	....	13·13	.... 12·86
$C^{28}N^3H^{15}O^2$,HCl........	277·4	....	100·00	.... 97·00

Nitrate. — Nitric acid combines with hydrocyanharmaline, forming a salt which is, oleaginous at first, but solidifies after some time to a crystalline mass. Finely divided hydrocyanharmaline mixed with a large quantity of water, dissolves on addition of nitric acid, to a clear liquid, which deposits after a while crystals of nitrate of hydro-cyanharmaline, and presently also of nitrate of harmaline.

Cold concentrated *acetic acid* gradually dissolves hydrocyan-harmaline; but the acetate cannot be obtained in the solid form from the solution, the yellow colour of which seems to indicate that the harmaline exists in it no longer in combination with hydrocyanic acid.

Hydrocyanharmaline dissolves sparingly in cold, more abundantly in hot *alcohol.*

Oxynitroazo-nucleus $C^{26}N^2XH^{11}O^2$.

Nitroharmaline.

$$C^{26}N^3H^{13}O^6 \;=\; C^{26}N^2XH^{11}O^2,H^2.$$
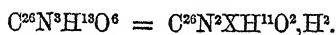
FRITZSCHE. See references 4 to 7, pages 103, 104.

Chrysoharmine. Nitroharmalidine.

Formation. By the action of nitric acid on harmaline.

Preparation. 1. Two parts of water are poured upon 1 pt. of harmaline; enough acetic acid is added to dissolve the latter; and the solution is poured in a fine stream into 24 pts. of boiling nitric acid of sp. gr. 1·120. As soon as the stormy evolution of red fumes, which takes place on mixing the liquids, has subsided, the lamp is re-moved; the liquid is cooled as quickly as possible, and excess of alkali is added, whereby nitroharmaline is precipitated, and a resin formed at the same time is kept in solution. The washed precipitate is triturated with dilute acetic acid, and chloride of sodium is added to the filtered solution, whereby hydrochlorate of nitroharmaline is precipitated; this is dissolved in lukewarm water, and nitroharmaline is precipitated from the solution by an alkali. — 2. Six to eight parts alcohol of 80 per cent. are poured upon 1 pt. harmaline, and 2 pts. oil of vitriol added; when the whole is dissolved, 2 pts. of moderately diluted nitric acid are added, and the mixture is placed in hot water. In

consequence of the action of the nitric acid upon the alcohol, violent ebullition of the liquid soon sets in, and must be stopped, after a short time, by rapidly cooling the mixture, whereupon nearly all the nitro-harmaline that has been formed is deposited as bisulphate. This product is washed with alcohol containing sulphuric acid, and dissolved in lukewarm water; dilute solution of caustic potash is added drop by drop to the solution when quite cold, until a permanent precipitate is produced, and the colour of the liquid has become pure golden yellow; foreign admixtures are thus separated, and the solution is then quickly filtered into a small quantity of acid. The feebly acid solution is warmed to 40° or 50°, and an excess of caustic potash or ammonia is added all at once with constant stirring; a crystalline precipitate of nitroharmaline is thus formed almost instantly. It can be obtained in somewhat larger crystals by recrystallisation from boiling water. Crude nitroharmaline may also be purified by precipitating its solution in sulphuric acid by means of common salt or nitrate of soda, dissolving the precipitated hydrochlorate or nitrate in cold water, and throwing down the nitroharmaline from the filtered solution. If harmaline or harmine is still present, the product is stirred up with water to a mud, and excess of concentrated aqueous sulphurous acid is added, whereby the whole is dissolved; after a while, however, the bisulphate of nitroharmaline separates out almost completely, while harmine and harmaline remain dissolved. The product is washed with dilute sulphurous acid, dissolved in warm water, and the solution precipitated by excess of alkali.

Properties. Small, orange-yellow prisms, which melt at 120°, often at lower temperatures, to a brown resin, and solidify again on cooling.

						Fritzsche. *mean.*		
						earlier.		*later.*
26	C	156	....	60·23	....	61·12	....	60·15
3	N	42	....	16·22	......	15·27		
13	H	13	....	5·02	....	5·14	....	4·92
6	O	48	....	18·53	....	18·47		
$C^{26}N^2XH^{13}O^2$		259	... .	100·00	... ...	100·00		

Decompositions. 1. Boiling concentrated *nitric acid* converts nitro-harmaline into nitroharmine. — 2. On heating the *bichromate*, a violent decomposition sets in, whereby a peculiar base is produced. — 3. *Hydrocyanic acid* converts it into hydrocyannitroharmaline.

Combinations. Dissolves in cold *water* to a very slight extent, colouring it yellow; it dissolves more readily in boiling water.

With *acids* it forms yellow, crystallisable *salts*, resembling those of harmaline. The neutral salts are decomposed by boiling their solutions; the basic salts are decomposed by merely standing in the air, and acquire a greenish-yellow colour, a dark-coloured substance precipitable by alkali being formed at the same time. Alkali added to the salts of nitroharmaline in quantity less than sufficient for complete decomposition, separates the base in the form of an oil or resin which solidifies only on standing. — Nitroharmaline dissolves abundantly in warm solution of sal-ammoniac, and displaces ammonia on boiling.

Sulphite of Nitroharmaline. — Freshly precipitated nitroharmaline dissolves abundantly in aqueous sulphuric acid, and separates almost completely, after some time, as bisulphite. — Sparingly soluble in water, still less in aqueous sulphuric acid.

Sulphate. — a. *Mono-acid.* — The aqueous solution of neutral acetate of nitroharmaline is saturated with sulphate of ammonia; or cold dilute sulphuric acid is digested with excess of nitroharmaline, and allowed to evaporate at the common temperature. Easily soluble in water.

b. *Biacid.* — Nitroharmaline is dissolved in boiling alcohol mixed with a great excess of sulphuric acid, and the solution is allowed to cool; or it is dissolved in excess of oil of vitriol and the dark brown-red solution is poured drop by drop into cold water with constant stirring, and the crystalline powder which separates is washed with water. — Bright yellow crystals, difficultly soluble in water.

				Fritzsche.
$C^{26}N^3H^{13}O^6$	259	....	72·54	.... 72·77
$2SO^3$	80	....	22·42	.... 21·98
$2HO$	18	....	5·04	.... 5·25
$C^{26}N^2XH^{13}O^2,2HO,2SO^3$	357	....	100·00	.... 100·00

Hydriodate and *Hydrobromate of Nitroharmaline.* — Obtained by double decomposition. Crystals very similar to the hydrochlorate.

Hydrochlorate. — 1. Nitroharmaline is covered with alcohol, a great excess of hydrochloric acid is added, the mixture is heated until the whole is dissolved and then allowed to cool. — 2. Aqueous acetate of nitroharmaline is precipitated by excess of hydrochloric acid or chloride of sodium. — Small, yellow crystals soluble in water and alcohol, insoluble in hydrochloric acid or solution of chloride of sodium.

				Fritzsche.
$C^{26}N^3H^{13}O^6$	259	....	87·67	.... 87·11
HCl	36·4	....	12·33	.... 12·14
$C^{26}N^2XH^{13}O^2,HCl$	295·4	....	100·00	.... 99·25

Nitrate. — Acetate of nitroharmaline is precipitated with nitric acid or nitrate of soda; or freshly precipitated nitroharmaline is dissolved in hot dilute nitric acid, whence the salt separates on cooling. Yellow needles; rather difficultly soluble in pure water, and still less soluble in water containing nitric acid.

Bichromate. — On mixing solutions of nitroharmaline and of chromic acid or bichromate of potash, oily drops separate which soon solidify in the crystalline state. — Sparingly soluble in cold water, but dissolves more easily in boiling water, and to some extent in alcohol, without decomposition.

Chloromercurate. — When cold solutions of mercuric chloride and hydrochlorate of nitroharmaline are mixed together, yellow flocks separate, which soon solidify in the crystalline form. From hot solutions, larger needle-shaped crystals are obtained on cooling.

Nitroharmaline with Silver-oxide. — A perfectly neutral solution of

nitrate of nitroharmaline, mixed with ammonio-nitrate of silver; deposits a gelatinous, yellowish-red precipitate, which becomes somewhat denser if left in the liquid, and shrinks on drying to brown-red amorphous lumps.

				Fritzsche.
				mean.
$C^{26}N^3H^{13}O^6$	259	69·07		68·44
AgO	116	30·93		30·00
$C^{26}N^2XH^{13}O^2,AgO$	375	100·00		98·44

Nitrate of Nitroharmaline and Silver. — Obtained by mixing alcoholic nitroharmaline with nitrate of silver. Bright yellow flocks, made up of bright yellow, interlaced needles commonly mingled with dark orange-yellow granules.

Chloroplatinate — On mixing together solutions of hydrochlorate of nitroharmaline and platinic chloride, bright yellow flocks are precipitated, which soon change to microscopic crystals, of a darker colour, grouped in stars.

					Fritzsche.
					mean.
26	C	156	....	33·55	.... 34·16
3	N	42	....	9·03	
14	H	14	....	3·01	... 3·08
6	O	48	....	10·34	
3	Cl	106·2	....	22·84	
	Pt	98·7	....	21·23	.... 21·09
$C^{26}N^2XH^{13}O^2,HCl,PtCl^2$		464·9	....	100·00	

Hydroferrocyanate. — Small bright brown feathery crystals, composed of smaller needles. Very difficultly soluble.

Hydroferridcyanate. — Separates in oily drops, which change in the course of a few moments to a yellow crystalline powder, on mixing solutions of ferridcyanide of potassium and a salt of nitro-harmaline.

Hydrosulphocyanate. — Bright yellow, microscopic needles, rather difficultly soluble in water.

Acetate. — Nitroharmaline dissolves easily in acetic acid. By evaporation at the ordinary temperature, the salt is obtained in the crystalline form.

Oxalate. — Nitroharmaline dissolves easily in aqueous oxalic acid, and is not precipitated from its solutions by excess of oxalic acid. The salt is obtained crystallised by evaporation of its solutions.

Nitroharmaline dissolves with tolerable ease in cold *alcohol*, but much more easily in hot alcohol, crystallising on cooling. — It dissolves but little in cold, somewhat more in boiling, *ether*, and is not precipitated by ether from its cold saturated alcoholic solution. — Dissolves abundantly in hot *volatile* and *fatty oils*, separating again on cooling. From the solution in warm *rock-oil*, there separate, together with orange-yellow crystals of nitroharmaline, bright yellow needles containing 5·6 to 6·31 p. c. rock-oil, smelling faintly of rock-oil, and unaltered at 100°. They split up into nitroharmaline and rock-oil, slowly when boiled with water, more quickly by contact with acids or alcohol.

Hydrocyannitroharmaline.

$$C^{28}N^4H^{14}O^6 \ = \ C^{26}N^2XH^{13}O^2,HCy.$$
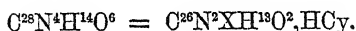
Fʀɪᴛᴢꜱᴄʜᴇ. See references 5 and 6, page 104.

Separates on cooling from a solution of nitroharmaline in warm alcoholic hydrocyanic acid, or when a mixture of acetate of nitroharmaline and excess of hydrocyanic acid is left to stand. — It is also obtained by mixing together cold aqueous salts of nitroharmaline and excess of hydrocyanic acid, and adding ammonia; it then separates at first as a jelly, but soon becomes crystalline.

Yellow needles, unalterable in dry air; smells of ammonia in damp air.

		at 100°.		Fritzsche.
$C^{26}N^2XH^{13}O^2$	 259	....	90·56	
HCy	 27	....	9·44	.... 8·85
$C^{26}N^2XH^{13}O^2,HCy.$	286	....	100·00	

Splits up when boiled with *water* into hydrocyanic acid and nitroharmaline. — Decomposed by concentrated *ammonia* and by *potash-ley*, acquiring a darker colour.

Dissolves in *oil of vitriol* at ordinary temperatures to a brown-yellow liquid, which deposits needles of sulphate of hydrocyannitroharmaline when dropped into a small quantity of water. These needles decompose when washed.

Primary Nucleus C²⁶H¹⁸; *Oxygen-nucleus* C²⁶H¹⁴O⁴.

Filicic Acid.

$$C^{28}H^{14}O^8 \ = \ C^{26}H^{14}O^4,O^4?$$
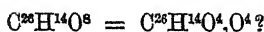
E. Lᴜᴄᴋ. *Ann. Pharm.* 54, 119 ; *Jahrb. pr. Pharm.* 22, 129.

Occurrence. In the roots of *Aspidium filix mas.*

Preparation. 1. Well preserved roots, which are still green when broken, are coarsely powdered and repeatedly exhausted with warm ether free from alcohol; the ether is distilled off from the extract so far that the residue has the consistence of olive-oil when cold; it is then allowed to stand for several days, whereupon yellow crusts of filicic acid are deposited on the sides of the vessel. This product is collected on a filter, washed with small quantities of a mixture of equal volumes of absolute alcohol and ether, then with a mixture of 2 pts. alcohol and 1 pt. ether, until the residue has become bright lemon-yellow, and crystallised from boiling ether; and the crystals are washed with a little ether-alcohol. — A still better method is to wash the yellow crusts only once with ether-alcohol, then press them between

filter-paper, dissolve in alcohol of 60° warmed to 35°, and then add aqueous ammonia until a turbid solution is produced. The liquid is quickly filtered and allowed to flow at once into dilute hydrochloric acid; and the precipitate is washed with water and then with warm alcohol of 80 p. c. as long as this liquid is coloured by it. — 2. The ethereal extract of the fern-root is diluted with ether-alcohol, then with 2 measures of water at 40° and $\frac{1}{2}$ measure of aqueous ammonia, or so much that the liquid smells of ammonia, and the whole is shaken. After standing, the lower brown layer is separated from the supernatant oil; it is filtered and precipitated with dilute hydrochloric acid, which throws down an abundant precipitate that quickly balls together to a soft plaster. This is kneaded with warm water and crystallised from boiling absolute alcohol; and the crystals are washed with alcohol of 80 p. c., and purified by solution in ammonia and precipitation by acid, as in 1.

Properties. Small, greenish-yellow, rhombic laminæ, or light, bright yellow crystalline powder. Has a faint smell, and a slight, nauseous taste. Becomes electric when rubbed. Melts at 161°, and solidifies on cooling to an amorphous, greenish-yellow, transparent mass. Its ethereal solution has an acid reaction.

Calculation according to Luck.				Luck.		
26 C 156	....	64·20	....	63·57	to	64·78
15 H 15	....	6·17	....	6·47	„	6·30
9 O 72	....	29·63	....	29·96	„	29·92
$C^{26}H^{15}O^9$........ 243	....	100·00	....	100·00		

Therefore perhaps $C^{26}H^{14}O^8,HO$.

Decompositions. 1. When *heated*, it yields an oily distillate smelling of butyric acid. — 2 *Burns* with luminous flame when heated on platinum-foil, and leaves a shining charcoal. — 3. Dissolves in fuming *oil of vitriol* at common temperatures to a brown liquid, from which, when it has stood only a short time, water separates filicic and filimelisi-sulphuric (xv. 26) acids, but only the latter acid when it has stood for 2 or 3 hours, butyric acid being formed at the same time. — Common oil of vitriol seems to act similarly. — 4. Dry *chlorine* converts it into chlorofilicic acid, with evolution of hydrochloric acid; chlorine passed into the aqueous solution converts it into terchlorofilicic acid. — 5. Filicic acid quickly assumes a dark brown-yellow colour when heated with aqueous *ammonia* or *caustic potash*, and, in absence of air, is converted into filimelisic acid; if air has access, it takes up oxygen and becomes filipelosic acid (xv. 26). When heated with lumps of potash-hydrate it gives off a smell of amber and mint. — 6. The soda-salt reduces aqueous *nitrate of silver* by long contact.

Combinations. Does not dissolve in *water*. With *salifiable bases* it forms the *filicates.* According to Luck, the acid then takes up 1 at. water additional, so that the formula of the lead-salt is $C^{26}H^{16}O^{10},PbO$.

Filicate of Soda. — The acid is digested with aqueous carbonate of soda at 60°; the bicarbonate so produced is precipitated with absolute alcohol, and the solution is evaporated in vacuo over oil of vitriol. It forms a gummy mass.

Aqueous filicate of soda precipitates the solutions of the following salts: chlorides of *barium* and *calcium* slightly, yellowish white and flocculent; chlorides of *magnesium, aluminum,* and *glucinum,* copiously, white; chloride of *cobalt,* flesh-coloured; chloride of *nickel,* bright apple-green; chloride of *manganese,* white; *ferrous chloride,* dark red-brown; *ferric chloride,* cinnamon-coloured; *cupric chloride,* and *chromic chloride,* green; *mercuric chloride,* slightly white; *platinic chloride,* dirty yellow.

Filicate of Lead. — Dilute aqueous filicate of soda is precipitated with sugar of lead, and the yellowish-white, curdy precipitate is dried at the common temperature, or in vacuo. — At 100°, it takes up oxygen and becomes darker coloured. — Sugar of lead precipitates from alcoholic filicate of soda mixed with acetic acid, other salts containing smaller and variable proportions of lead.

			Calculation according to Luck.		Luck. *mean.*
26	C	156	42·91		43·12
16	H	16	4·40		4·47
10	O	80	22·00		21·69
	PbO	112	30·69		30·72
	$C^{26}H^{16}O^{10}$,PbO	364	100·00		100·00

Filicic acid dissolves but sparingly in aqueous *alcohol,* but is soluble in boiling absolute alcohol. — It is only slightly more soluble in boiling than in cold *ether,* but dissolves more readily in presence of fat oils. Very easily soluble in *sulphide of carbon* and in *fat* and *volatile oils* (Luck).

Oxychlorine-nucleus $C^{26}ClH^{13}O^4$.

Chlorofilicic Acid.

$$C^{26}ClH^{13}O^8 = C^{26}ClH^{13}O^4,O^4?$$
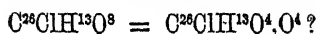
Luck. *Jahrb. pr. Pharm.* 22, 136.

When dry chlorine is passed over filicic acid contained in a bulb-tube, a gentle heat being applied at the end of the operation, heat is evolved and hydrochloric acid formed, and there is produced a turpentine-like mass which, when dissolved in alcohol of 80 p. c. and abandoned to spontaneous evaporation, is deposited in yellow-brown drops. These are washed with water and dried at the common temperature.

Properties. An amorphous mass, yielding a yellow powder, and caking together at a gentle heat into a transparent resin. It reddens litmus when dissolved in alcohol.

<table>
<thead>
<tr><th></th><th colspan="2">Calculation according to Luck.</th><th>Luck.
in vacuo,
over oil of vitriol.</th></tr>
</thead>
</table>

26 C	156	. ...	54·17	. .... 54·67
15 H	15	...	5·23	. . . 5 28
Cl	35·5		12·36	.... . 12·19
10 O	80		27 91	. 27·86
$C^{26}H^{15}ClO^{10}$ 286 5			.... 100 00	.... 100·00

Perhaps $C^{2b}ClH^{13}O^8,2HO$?

Becomes coloured when heated with aqueous *carbonated* or *caustic alkalis*, and forms alkaline chloride.

Insoluble in *water ;* dissolves in alkaline liquids with yellow colour. The solution of chlorofilicate of soda, obtained by dissolving the acid in aqueous carbonate of soda, and freed from excess of carbonate by precipitation with absolute alcohol, precipitates *ferrous* and *ferric chlorides* dark brown, and produces a faint turbidity, soluble in nitric acid, with *nitrate of silver.*

Lead-salt. — Obtained by precipitating the alcoholic acid with sugar of lead. Bright clay-coloured powder. Contains 39·12 p. c. C., 3·90 H., and 28·27 PbO., and is therefore $C^{26}H^{25}ClO^{10}$, PbO (calculation : 39·20 p. c. C., 3·76 H., and 28 03 PbO). (Luck.)

Chlorofilicic acid is soluble in *alcohol, ether, sulphide of carbon,* and *fat oils* (Luck).

Oxychlorine-nucleus $C^{26}Cl^3H^{11}O^4$?

Terchlorofilicic Acid.

$$C^{26}Cl^3H^{11}O^8 \ = \ C^{26}Cl^3H^{11}O^4,O^4 \ ?$$
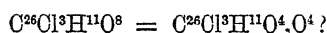
LUCK. *Jahrb. pr. Pharm.* 22, 137.

Chlorine gas is passed into water in which filicic acid is suspended until free chlorine is still present in the liquid after twenty-four hours ; the product is collected, washed with water, dried, and dissolved in alcohol. The solution, abandoned to spontaneous evaporation, leaves a residue of amorphous terchlorofilicic acid, which must be washed with water.

It forms an amorphous mass, yielding a yellow powder, fusible in hot water, and having a faint bitter taste. Reacts acid.

	Calculation according to Luck.			Luck. in vacuo, over oil of vitriol.	
26 C	156	....	43·91	....	43·80
13 H	13	....	3·65	....	3·58
3 Cl	106·5	....	29·90	....	29·81
10 O	80	....	22·54	....	22·81
$C^{26}H^{13}Cl^3O^{10}$....	355·5	....	100·00	....	100·00

Perhaps $C^{2b}Cl^3H^{11}O^8,2HO$?

Evolves hydrochloric acid when *heated*, and leaves a residue of charcoal.

Insoluble in *water*.

Lead-salt. — Obtained like chlorofilicate of lead (page 129), as a bright clay-coloured precipitate, and contains, when dried in vacuo over oil of vitriol, 33·31 p.c. C., 2·83 H., and 24·08 PbO., and is therefore $C^{28}H^{12}Cl^3PbO^{10}$ + HO (calculation : 33·42 p. c. C., 2·78 H., and 23·90 PbO). (Luck.)

The acid dissolves in *alcohol*, in *ether*, and in *oils* both *fat* and *volatile*.

Oxyazo-nucleus $C^{26}NH^{11}O^6$.

Cotarnine.

$$C^{26}NH^{13}O^6 = C^{26}NH^{11}O^6, H^2.$$
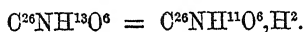
(More correctly $C^{24}NH^{11}O^6$.)

Wöhler.   *Ann. Pharm.* 50, 19.
Blyth.   *Ann. Pharm.* 50, 36.
Anderson.   *Edinb. Royal Soc. Trans.* 20, 3, 347 ; *Chem. Soc. Qu. J.* 5, 257 ; abstr. *Ann. Pharm.* 86, 179 ; *J. pr. Chem.* 57, 358 ; *Lieb. Kopp's Jahresb.* 1852, 537.
Matthiessen & Foster.   *Phil. Trans.* 1863, 348 ; *Chem. Soc. J.* [2] 1, 342 ; abstr. *Proc. Roy. Soc.* 11, 57 ; *Ann. Pharm. Suppl.* 1, 331 ; *Proc. Roy. Soc.* 12, 503.

Discovered by Wohler in 1844. — It belongs, according to Matthiessen & Foster, to the compounds containing 24 at. carbon ; but the preparation of this work was too far advanced to admit of its being described in that connection.

Formation. From narcotine. 1. By boiling it with peroxide of manganese and dilute sulphuric acid (Wöhler). — 2. By boiling hydrochlorate of narcotine with excess of bichloride of platinum (Blyth). — 3. By the action of dilute nitric acid on narcotine (Anderson). In all cases opianic acid (xiv. 427) is formed at the same time.

Preparation. 1. When narcotine is decomposed by peroxide of manganese and sulphuric acid, as for the preparation of opianic acid (xiv. 427) the red-yellow mother-liquor remaining after separation of the opianic acid, contains cotarnine in solution, which can be precipitated by (mercuric chloride or) bichloride of platinum. The precipitate is purified by washing with cold water and recrystallisation from boiling water containing hydrochloric acid ; it is then pulverised, heated with water to boiling, and decomposed by a current of hydrosulphuric acid. The solution of hydrochlorate of cotarnine filtered from the sulphide of platinum is mixed with excess of baryta-water and evaporated to dryness, and the cotarnine is dissolved out from the residue in which it is contained, together with carbonate of baryta and chloride of barium, by means of alcohol (Wöhler). — 2. In the

decomposition of narcotine by bichloride of platinum, as described at page 427, vol. xiv., crystals of chloroplatinate of cotarnine separate from the dark-red liquid after half-an-hour's boiling, while opianic and hemipinic (xiv. 430) acids remain in solution. The crystals are washed with water, heated to boiling with aqueous ammonia, decomposed by leading hydrosulphuric acid into the liquid, and the whole is evaporated to dryness. The residue is treated with water acidulated by hydrochloric acid, to decompose the compound of bisulphide of platinum and sulphide of ammonium, the liquid filtered, and the greater part of the cotarnine precipitated from the filtrate by addition of potash. The remainder, which is kept in solution by the ammonia contained in the liquid, is separated by evaporation. The whole quantity of cotarnine so obtained is purified by treating its solution in hydrochloric acid with animal charcoal and precipitating with potash (Blyth). — 3. Cotarnine is also obtained by boiling narcotine with nitric acid, as described under B, vol. xiv. page 423 (Anderson). — ¶. Matthiessen & Foster give the following process for the preparation of cotarnine : 2 pts. of narcotine is dissolved in a mixture of 30 pts. water and 3 pts. sulphuric acid ; the solution is heated to boiling, and 3 pts. peroxide of manganese in fine powder is added to it as quickly as possible, care being taken that it does not cause the liquid to boil over ; the mixture is then quickly filtered through a funnel surrounded by boiling water. The mother-liquor, drained off from the opianic acid which crystallises from the filtrate on cooling, is mixed with a quantity of milk of lime, sufficient to neutralise the free sulphuric acid and to precipitate the greater part of the manganese, then with excess of carbonate of soda; the whole is next heated to boiling for a few minutes, and filtered; the filtrate is neutralised with dilute sulphuric acid, evaporated rapidly to a small bulk, allowed to cool completely, poured off from any sulphate of soda that may have crystallised out, and finally mixed with excess of strong potash-ley whereby the cotarnine is precipitated. The product so obtained may be dissolved in hydrochloric acid and decolorised with animal charcoal if necessary.¶

Properties. Crystallised cotarnine (p. 132) loses water at 100°, and melts to a brown mass (Blyth). Reacts feebly alkaline. Tastes very bitter (Wohler).

	a.				*b.*			Blyth. *Dried.*
24 C	144	....	65·76	26 C	156	....	67·53	65·95
N	14	....	6·39	N	14	....	6·06	
13 H	13	....	5·93	13 H	13	....	5·63	6·39
6 O	48	....	21·92	6 O	48	....	20·78	
$C^{24}NH^{13}O^6$	219	....	100·00	$C^{26}NH^{13}O^6$	231	....	100·00	

a according to Matthiessen & Foster; the formula $C^{26}NH^{13}O^6$ (*b*) was proposed by Gerhardt (*Précis de Chimie organique*, 2, 189, 258, Paris, 1845) and Laurent (*N. Ann. Chim. Phys.* 19, 370; *Ann. Pharm.* 62, 104). Wohler gave the formula $C^{26}NH^{15}O^5$; Blyth $C^{25}NH^{13}O^6$.

Decompositions. 1. Melts when *heated* and chars, giving off a disagreeable smell (Wohler). — 2. By gently warming cotarnine with very dilute *nitric acid*, cotarnic acid (p. 134) and nitrate of methylamine are obtained, $C^{24}NH^{13}O^6 + 4HO = C^{22}H^{12}O^{10} + C^2NH^5$ (Matthiessen & Foster.)

к 2

—If cotarnine is dissolved in nitric acid diluted with two measures of water, and the solution boiled with addition of strong nitric acid (whereupon nitrous fumes are evolved) until a sample deposits crystals when mixed with ether-alcohol, apophyllic acid (xiii. 154) is produced. The mother-liquor of this acid yields, by dry distillation, a syrup, which evolves methylamine, ethylamine (bimethylamine? Kr.), and perhaps other bases when treated with potash. (Anderson). Cotarnine dissolves with dark red colour in concentrated nitric acid (Blyth); and is converted by it, on boiling, into oxalic acid (Anderson).

On one occasion Anderson obtained, at the same time as apophyllic acid, yellow acid needles, melting to a yellow oil, and solidifying to a crystalline mass on cooling. This was soluble in water, and contained one time 55·80 p. c C., and 3·94 H.; another time, when dried at 100°, it contained 61·21 p. c. C., 4·16 N., 3·94 H., and 30·66 O., which latter numbers correspond to the formula $C^{36}NH^{13}O^{14}$ (Anderson).

¶ 3. Cotarnine, heated in a sealed tube with aqueous *hydrochloric* (hydriodic or sulphuric) *acid*, yields hydrochlorate of cotarnamic acid (p. 134) and chloride of methyl: $C^{24}NH^{13}O^6 + 2HO = C^{22}NH^{13}O^8,HCl + C^2H^3Cl$ (Matthiessen & Foster). — 4. Distilled with caustic *potash* it yields ammonia and methylamine, but apparently no bi- or ter- methylamine (Matth. & Foster). ¶ — 5. Heated with absolute alcohol and *iodide of ethyl*, it is converted into hydriodate of cotarnine (see below), without formation of an ethyl-cotarnine (How).

Combinations. — *With Water.* — *Crystallised Cotarnine.* — Colourless needles, grouped in stars (Blyth), yellowish or buff (Matthiessen & Foster). Loses 7·22 to 7·51 p. c. water at 100° (Blyth), 7·45 p. c. (Matthiessen & Foster: 2 at. = 7·59 p. c.). Wöhler obtained (hydrated?) cotarnine as a deep yellow mass of radiating crystals.

Over oil of vitriol.

a.

24	C	144	60·76
	N	14	5·90
15	H	15	6·33
8	O	64	27·01

$C^{24}NH^{13}O^6,2HO$ .... 237 .... 100·00

b.

					Blyth.	Matthiessen & Foster.	
26	C	156	62·65		61·41	60·84	60·55
	N	14	5·62		5·52	5·82	5·91
15	H	15	6·02		6·38	6·53	6·50
8	O	64	25·71		26·69	26·81	27·04

$C^{26}NH^{13}O^6,2HO$ .... 249 .... 100·00 .... 100·00 .... 100·00 .... 100·00

Cotarnine dissolves easily in *water* with deep yellow colour (Wöhler). It dissolves slightly in aqueous *ammonia*, not in *potash-ley*, and does not colour *ferric salts* (Blyth).

The *salts of cotarnine* are obtained by dissolving cotarnine in dilute acids; they are easily soluble. Aqueous cotarnine precipitates *cupric* and *ferrous salts* (Blyth).

Hydriodate of Cotarnine. — Obtained as a red-brown uncrystallisable oil, by heating finely powdered cotarnine with absolute alcohol and

iodide of ethyl to 100° in a sealed tube.   Insoluble in cold water; dissolves readily in hot water.   By treatment with nitrate of silver and then with hydrochloric acid, it is converted into hydrochlorate of cotarnine. (How.)

Hydrochlorate. — Long needles, having a silky lustre, losing 14·51 to 15·24 p. c. water at 100° (? 4 at. = 13·84 p. c.), and very soluble in water (Blyth).

		at 100°.			Blyth.
24	C	144	......	56·36	57·39
	N	14	......	5·48	
14	H	14	......	5·48	5·73
6	O	48	......	18·78	
	Cl	35·5	......	13·90	

$C^{24}NH^{13}O^6,HCl$ .... 255·5 .... 100·00

Chloromercurate. — Separates as a thick, pale yellow precipitate, which soon becomes crystalline, on mixing cold solutions of hydrochlorate of cotarnine and mercuric chloride; crystallises on cooling from warm dilute solutions in small yellow prisms.   Appears to be decomposed by recrystallisation.   A specimen, which was perhaps not quite pure, contained 37·95 p. c. Hg., 20·68 Cl., 2·52 N. (Wöhler: calculation for $C^{24}NH^{13}O^6,HCl,2HgCl$ = 38·06 p. c. Hg., 20·21 Cl., 2·66 N.).

Chloroplatinate. —Obtained, as described at page 130, in long red prisms; by precipitation of hydrochlorate of cotarnine with bichloride of platinum, as a lemon-yellow precipitate, resembling chloroplatinate of ammonia, and becoming red on drying. — Not decomposed by boiling with aqueous ammonia; appears to be decomposed by recrystallisation.   Slightly soluble in water (Wöhler, Blyth).

						Wöhler. *mean.*		Blyth. *mean.*
24	C	144	......	33·84	......	34·70	......	34·76
	N	14	......	3·29				
14	H	14	......	3·29	......	3·33	......	3·47
6	O	48	......	11·28				
3	Cl	106·5	......	25·03	......	24·09		
	Pt	99	......	23·27	......	22·80	......	22·89

$C^{24}NH^{13}O^6,HCl,PtCl^2$ .... 425·5 .... 100·00

How found 22·38 p.c. platinum; Matthiessen & Foster 23·10 to 23·31 p.c.

Hydrochlorate of cotarnine forms a splendid dark-red double salt with *terchloride of gold* (Blyth).

Dissolves readily in *alcohol* with deep yellow colour (Wöhler); with brown colour, and cannot be again obtained crystallised (Blyth).

Easily soluble in *ether*.   The solution in hydrochloric acid is precipitated by *tannic acid.*

Appendix to vol. xiv., p. 521.

Cotarnic Acid.

$$C^{22}H^{12}O^{10} = C^{22}H^{12}O^4,O^6.$$

MATTHIESSEN & FOSTER.   *Proc. Roy. Soc.* 11, 59; *Ann. Pharm. Suppl.* 1, 331.

Obtained, but not always, together with nitrate of methylamine, by gently heating cotarnine with very dilute nitric acid. — Perhaps identical with Anderson's hydrate of opianyl (xiv. 424).   Contains no nitrogen; its aqueous solution reacts strongly acid. — Easily soluble in *water;* gives no coloration with sesquichloride of iron.   Gives a white precipitate with *acetate of lead,* insoluble in excess of acetate of lead.

Cotarnate of Silver. — Nitrate of silver gives, with the aqueous acid, a precipitate which is slightly soluble in hot water.

				Matth. & Foster.
				mean.
22 C	 132	....	30·14	....	29·67
10 H	 10	....	2·27	....	2·17
2 Ag	 216	....	49·32	....	49·24
10 O	 80	....	18·27	....	18·92
$C^{22}H^{10}Ag^2O^{10}$ 438	....	100·00	....	100·00

The acid dissolves sparingly in *alcohol,* and is precipitated from the solution by ether.

¶.   *Oxyamidogen-nucleus* $C^{22}AdH^{11}O^4$.

Cotarnamic Acid.

$$C^{22}NH^{13}O^8 = C^{22}AdH^{11}O^4,O^4.$$
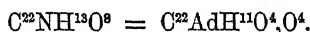
MATTHIESSEN & FOSTER.   *Phil. Trans.* 1863, 360; abstr. *Proc. Roy. Soc.* 12, 503.

Precipitated as an orange-red crystalline powder on cautiously adding aqueous ammonia or carbonate or sulphite of soda to the aqueous solution of hydrochlorate of cotarnamic acid. — Dissolves with orange colour in excess of aqueous alkali, the solution rapidly becoming dark brown by exposure to air.

Combinations.   Dissolves sparingly in cold, somewhat more abundantly in boiling *water,* a very small quantity imparting an intense orange colour to a large bulk of water.

Hydrochlorate of Cotarnamic Acid. — Formed, together with chloride methyl, by heating cotarnine with three times its weight of strong

aqueous hydrochloric acid to about 140° in a sealed tube (p. 132), or by the action of dilute hydrochloric acid on cotarnamic acid.

Pale yellow tufts of small silky needles.

					Matth. & Foster.
					mean.
22 C		132	....	50·87	....	49·94
N		14	....	5·40	....	5·73
14 H		14	....	5·40	....	5·70
8 O		64	....	24·65	....	24·61
Cl		35·5	....	13·68	....	14·02
$C^{22}AdH^{11}O^{4},HCl$		259·5	....	100·00	....	100·00

Partially decomposed, with separation of cotarnamic acid, when dissolved in pure water; dissolves without decomposition in water containing a trace of hydrochloric acid, giving a lemon-yellow solution which becomes dark green by exposure to the air. — Nitric acid dropped into the boiling aqueous solution, causes it to assume a deep opaque crimson colour when seen by reflected light, and transparent orange by transmitted light; after some minutes, slight effervescence takes place, and the solution remains transparent, but of a darker orange colour. — Evaporated nearly to dryness with excess of dilute sulphuric acid, it acquires a magnificent crimson colour, which disappears on addition of water, but is restored on again evaporating. — Reduces nitrate of silver added in excess to the hot solution. — Ammonia, carbonate of soda, or sulphite of soda, added to the aqueous solution, throw down cotarnamic acid, easily soluble in excess of the first.

Hydrochlorate of cotarnamic acid dissolves very readily in boiling water, much less easily in cold water. It is slightly soluble in alcohol; insoluble in ether. ¶.

Conjugated Compounds of Cotarnine.

Narcotine.

$$C^{44}NH^{23}O^{14} \text{ or } C^{46}NH^{25}O^{14}.$$
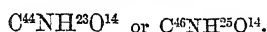
DEROSNE. *Ann. Chim.* 45, 271; *A. Tr.* 12, 1, 223.
ROBIQUET. *Ann. Chim. Phys.* 5, 275; *Gilb.* 57, 163. — *J. Pharm.* 17, 637; *Ann. Pharm.* 2, 267. — *J. Chim. méd.* 9, 66; *Ann. Chim. Phys.* 51, 226; *Ann. Pharm.* 5, 83.
SERTUEBNER. *Gilb.* 59, 50.
DUMAS & PELLETIER. *Ann. Chim. Phys.* 24, 185.
MERCK. *Mag. Pharm.* 15, 147. — *J. Pharm.* 16, 380. — *N. Tr.* 20, 1, 134. — *Ann. Pharm.* 21, 202.
GEIGER. *Mag. Pharm.* 17, 221.
DUFLOS. *Schw.* 61, 217.
BRANDES. *Ann. Pharm.* 2, 274.
PELLETIER. *Ann. Chim. Phys.* 50, 240; *Ann. Pharm.* 5, 169.
LIEBIG. *Ann. Pharm.* 6, 35; 26, 51; *Pogg.* 21, 30.
COUERBE. *Ann. Chim. Phys.* 59, 159; *Ann. Pharm.* 17, 174.
REGNAULT. *Ann. Pharm.* 26, 27; 29, 60; *J. pr. Chem.* 16, 273.
WÖHLER. *Ann. Pharm.* 50, 1; *J. pr. Chem.* 31, 420; *Pogg.* 61, 522.

BLYTH. *Ann. Pharm.* 50, 29 ; *Phil. Mag. J.* 25, 363.

WERTHEIM. *Ann. Pharm.* 70, 71. — *Ann. Pharm.* 73, 208 ; *Wien. Akad. Ber.* 4, 8 ; *Chem. Gaz.* 1850, 141. — *Wien. Akad. Ber.* 6, 109 ; *J. pr. Chem.* 53, 180 and 431 ; *Pharm. Centr.* 1851, 918 ; *N. J. Pharm.* 19, 388. — *Gerhardt, Traité* 4, 67.

ANDERSON. *Edinb. Royal Soc. Trans.* 20, 3, 347 ; *Ann. Pharm.* 86, 179 ; *J. pr. Chem.* 57, 358.

HOW. *Edinb. Royal Soc. Trans.* 21, 1, 27 ; *Ann. Pharm.* 92, 337 ; *J. pr. Chem.* 63, 300 ; *Chem. Centr.* 1855, 26.

MATTHIESSEN & FOSTER. *Phil. Trans.* 1863, 345 ; abstr. *Chem. Soc. J.* [2] 1, 342 ; *Proc. Roy. Soc.* 11, 55 ; *Ann. Pharm. Suppl.* 1, 330 ; *Rép. Chim. pure*, 3, 282 ; *Zeitschr. Chem. Pharm.* 4, 226 ; *Bull. Soc. Chim. Paris*, 1862, 22 ; further, *Proc. Roy. Soc.* 12, 501.

The *opian* of the 3rd German edition of Gmelin's *Handbuch*. *Sel d'opium* of Derosne. *Narcotine principle of opium.* — Discovered in 1803 by Derosne, and at first considered almost identical with morphine. Serturner at one time regarded it as basic meconate of morphine, but afterwards Robiquet and also Serturner himself showed that the two substances were distinct.

Occurrence. In opium (*Handbuch*, viii. *Phytochem.* 40) ; according to Pelletier in the free state (that is, not combined with acids) ; according to Serturner and Berzelius as a salt (decomposable by the solvent medium). — The proportion of narcotine in Bengal opium varies from 0·75 to 6 p.c. (O'Shaughnessy). Fresh poppy-sap collected in Bengal contained 1·635 p.c. narcotine, after separation of water 4 p. c. ; the same sap dried at 96°, or slowly evaporated in open dishes, contained, after removal of water, 3·8 and 3·6 p. c. (Eatwell, *Pharm. J. Trans.* 11, 269, 306 and 359 ; *Ann. Pharm.* 84, 385). The proportion of narcotine which the undermentioned varieties of opium respectively contain is as follows :—Smyrna opium, 6·5 to 9·6 p. c. (Mulder), 1·30 p. c. (Schindler) ; Egyptian opium, 2·68 p. c. ; opium from Constantinople, 3·47 p. c. (Schindler) ; Oriental opium (dry), 7·5 p. c. (Biltz). Opium collected from white poppies at Erfurt in 1829, contained 3·3 p. c. narcotine, that collected from blue poppies in 1829 contained 9 5 ; in 1830 it contained 6 25 p. c. narcotine (Biltz, *N. Tr.* 23, 1, 245 ; *Berz. Lehrb.* 3 *Aufl.* 7, 285). — The ripe capsules of the blue-seeded poppy contain narcotine (Winckler, *Repert.* 59, 17) ; the poppy-heads when not quite ripe contain narcotine and codeine (or perhaps thebaine), but no morphine (Winckler, *Repert.* 53, 289). French opium contained no narcotine but a large quantity of morphine (Pelletier, *J. Pharm.* 21, 570). — The deposit which forms in *Laudanum liquidum Sydenhami* by keeping, contains a relatively large quantity of narcotine (Bihot, *Pharm. Viertelj.* 6 ; *N. Br. Arch.* 95, 71).

Preparation. Narcotine is commonly obtained as a bye-product in the preparation of morphine. 1. When opium is exhausted with cold water for the purpose of preparing morphine, the greater part of the narcotine remains, as a general rule, in the residue ; but, according to Robiquet, when the characters of the opium are different, the whole, or most of it, may pass into solution with the morphine.

a. The residue of the opium which is insoluble in water, is exhausted with hydrochloric acid (or with alcohol) ; the narcotine is precipitated from the resulting solution by means of bicarbonate of soda ; the precipitate is exhausted with alcohol of 80 p. c. ; one-half or one-third of the alcohol is distilled off, and the residue is poured boiling hot into a flat vessel, wherein the narcotine crystallises, after from two to four hours. The crystals are to be washed with cold alcohol, and recrystallised from boiling alcohol (*Berz. Lehrb.* 6, 289).

b. The extract of opium, prepared with cold water, is evaporated to a thick syrup, allowed to cool, and mixed up with 5 or 6 parts water ; whereupon narcotine is deposited as a black-brown, sandy, crystalline mass, a further quantity of which can be obtained by

evaporating and redissolving the filtrate (Derosne). Caustic or carbonated alkalis extract the foreign colouring substances from this product, and leave nearly white narcotine (Wiggers). — Ether takes up narcotine, or narcotine together with foreign matters, from the extract obtained by exhausting opium with water, and evaporating. The ether is driven off, and the residual acid, brown, saline mass is dissolved in hot water or alcohol, decolorised with animal charcoal, and the narcotine precipitated from the cooled filtrate by ammonia.

2. If the opium has been exhausted with water containing hydrochloric acid, the narcotine may be precipitated from the extract by dissolving chloride of sodium therein. The liquid, which is at first milky, deposits, on standing, a brown, curdy precipitate, which is dissolved in dilute hydrochloric acid, and precipitated by potash-ley (Wittstock).

3. Opium is exhausted first with cold ether (which takes up the greater part of the fat and resin, together with a small quantity of narcotine), then repeatedly with boiling ether; the extracts obtained by hot ether are evaporated, and the residual narcotine is freed from adhering soft resin by repeated crystallisation from alcohol (Robiquet). — Serturner distills off ¾ of the ether from the ethereal extract of opium, whereupon the residue separates into a saline crust and mother-ley, both containing narcotine. He removes the resin from the former by means of heated oil of turpentine; washes with cold, and dissolves in boiling alcohol, and precipitates the narcotine from the solution (which reacts acid with litmus) by ammonia. — He evaporates the mother-ley, exhausts the residue with boiling water, and precipitates this solution also with ammonia. — The crystals of narcotine, which form on evaporating the ethereal extract of opium can also be separated mechanically from the precipitated resin, or by treatment with dilute hydrochloric acid and precipitation with ammonia, or by washing with cold ether (Brandes). In case they are mixed with crystals of meconin, the latter can be removed by boiling water (Merck). — On the preparation of narcotine for use in medicine, see O'Shaughnessy (*Repert.* 69, 94).

Purification. By solution in hydrochloric acid, precipitation with potash-ley, and recrystallisation of the washed precipitate from boiling alcohol.

Properties. Long needles, colourless, pearly-lustrous, and right rhombic prisms, often flat, often radiating (Serturner, Derosne). Crystalline form corresponds with that of opianine (p. 146) (Schabus). Heavier than water. Melts, when heated to 170°, like wax, and soaks into filter-paper, losing, at the same time (according to Pelletier & Dumas) 2 to 3 p. c. water, and solidifies at 130°, to a radiate mass when cooled slowly, or to a transparent, fissured resin when cooled quickly. — Odourless. Tasteless. — Neutral to vegetable colours. — Molecular rotatory power (xv. 245, footnote) to the left, $[\alpha]r = 130°·6$ or 151·4°; but not ascertainable with exactness on account of its slight solubility in cold alcohol and ether. On addition of acids, it acquires a rotatory power towards the right, the original rotatory power being brought back by neutralisation with ammonia. The rotatory power of acid solutions of narcotine was found by Bouchardat to vary according to the quantity and nature of the acid (Bouchardat, *N. Ann. Chim. Phys.* 9, 224. — *N. J. Pharm.* 23, 288; *J. pr. Chem.* 60, 118).

Less poisonous than morphine. Pure narcotine has no effect on human beings, even in doses of 120 grains; less than 140 grains does

not produce giddiness. Dissolved in acetic or hydrochloric acid, 20 to 70 grains produces giddiness, trembling, and sleeplessness. Thirty grains dissolved in acetic acid is a fatal dose for a dog (Orfila). Acts as a febrifuge (O'Shaughnessy).

	a.				b.	
44 C	264	63·92	46 C	276	64·63
N	14	3·39	N	14	3·27
23 H	23	5·57	25 H	25	5·85
14 O	112	27·12	14 O	112	26·25
$C^{44}NH^{23}O^{14}$	413	100·00	$C^{46}NH^{25}O^{14}$	427	100·00

	Liebig.	Pelletier.	Regnault.	A. W. Hofmann.
C	64·09	63·91	64·25	64·53
N	2·51	4·31	3·49	3·30
H	5·50	5·45	5·96	6·21
O	27·90	26·33	26·30	25·96
	100·00	100·00	100·00	100·00

Matthiessen & Foster.

	a. mean.	b.	c.	d.	e.	f. mean.
C	63·79	63·47	64·01	63·74	63·80	63·80
N	3·32					
H	5·81	5·73	5·71	5·77	5·75	5·71
O	27·08					
	100·00					

Varrentrapp & Will (*Ann. Pharm.* 39, 282) found 3·75 p. c., Mulder found 2·44 to 3·03 p. c. nitrogen. — Matthiessen & Foster analysed *a* narcotine from a mixture of various kinds of opium, *b* narcotine from Turkish opium, *c* from Egyptian opium, *d* from Persian opium, *e* from Egyptian opium, another sample, *f* from Turkish opium, another sample. — In place of the earlier formulæ of Liebig ($C^{48}NH^{24}O^{15}$ and $C^{40}NH^{20}O^{12}$), Regnault ($C^{44}NH^{23}O^{13}$), and Pelletier ($C^{34}NH^{17}O^{10}$), Blyth proposed the formula *b*. The decompositions of narcotine are still better explained by Matthiessen & Foster's formula, *a*, which contains the elements of cotarnine and of opianyl.

According to Wertheim there exist, in addition to the narcotine investigated by Wöhler and Blyth (named by Wertheim ethyl-narcotine), two other homologous bases, differing from this by containing 2 at. carbon and 2 at. hydrogen more and less respectively, and distinguishable by their yielding, when distilled with potash-hydrate, the former propylamine, the latter methylamine, while ethyl-narcotine yields ethylamine by the same treatment. He gave to these bases the formulæ $C^{44}NH^{23}O^{14}$ (methyl-narcotine), $C^{46}NH^{25}O^{14}$ (ethyl-narcotine : Wöhler and Blyth's narcotine), and $C^{48}NH^{27}O^{14}$ (propyl-narcotine). Hinterberger regards the base used by him for the preparation of the chloromercurate of narcotine (p. 144) as a fourth variety, containing C^2H^2 less than Wertheim's methylnarcotine. Matthiessen & Foster, on the other hand, found all the narcotines of the manufactories to have the same composition, and consider it more probable that one and the same narcotine (since, when distilled with hydriodic acid, it yields 3 at. iodide of methyl) may yield by distillation with potash-hydrate, now methylamine, now bimethylamine, and now termethylamine; which last would appear, according to this view, to have been mistaken by Wertheim for its isomer propylamine.

Decompositions. 1. When narcotine is *heated* in an oil-bath a few degrees above its melting point, it gradually acquires a deep red-yellow colour, and at about 220° it suddenly froths up strongly, evolves nearly pure ammonia, and solidifies to an exceedingly porous mass, consisting of humopic acid and a small quantity of a peculiar base different from narcotine and cotarnine. Hydrochloric acid extracts the base from this residue; water forms a yellow solution

containing the compound of the base with humopic acid, from which humopic acid is precipitated by acids (Wöhler).

The *new base* is precipitated from its hydrochloric acid solution by mercuric chloride or by bichloride of platinum, as a double salt, but rendered impure by a second product of decomposition, which colours the liquids and precipitates blue or blue-green, and produces a blue-black coloration with ferric chloride. The double salts, freed as far as possible from this product, are found to be soluble in boiling water, and are deposited on cooling, the mercury salt in small white, the platinum-salt in small reddish-yellow crystals. The latter froths up strongly when heated, and leaves 13·4 p. c. platinum as a soft, bulky skeleton (Wöhler).

Narcotine melts and froths when subjected to dry distillation, yielding carbonic acid and combustible gas, water, carbonate of ammonia, and empyreumatic oil, and leaves charcoal (Derosne).

2. When heated beyond its melting point in contact with the air, it is coloured purple, brown, and then black, gives out a dense brown smoke, takes fire, with vivid evolution of sparks, and *burns* with red, slightly smoky flame, leaving a soft, shining charcoal (Merck, Duflos, Winckler). The smell which it gives off is the same as that produced by quinine and meconin (Winckler). Narcotine takes fire on red-hot coals (Derosne). — 3. Heated with *water* in a sealed tube to 200°, it dissolves completely with red-yellow colour, giving a neutral solution which is coloured black-blue by ferric chloride (Wöhler). Heated with water to 240° or 260°, it yields propylamine (or rather termethylamine) (Reynoso, *Compt. rend.* 34, 799).

4. Dissolved in water in the form of a salt, narcotine is violently attacked by the *electric current*, in the same way as by hot concentrated nitric acid (Hlasiwetz & Rochleder, *Wien. Akad. Ber.* 5, 447).

5. Exposed to the vapour of *bromine*, it is coloured orange-yellow; in *iodine*-vapour, brown-yellow; in *chloride-of-iodine* vapour, vermilion-red to yellow (Donné, *J. Pharm.* 16, 372). The salts of narcotine are not coloured by aqueous *iodic acid* (Serullas, *Ann. Chim. Phys.* 43, 211).

In dry *chlorine* gas, narcotine quickly becomes red-brown; the mass is partially soluble in water with green colour, while a greenish-black residue remains. On leading chlorine into water in which narcotine is suspended, it acquires at first a flesh-red colour, then becomes darker, brown-red, dissolves entirely, and deposits brown flocks; while the liquid becomes greenish, and after filtering off the flocks, yields, when neutralised with ammonia, a small quantity of a beautiful green resin. The flocks, by washing with boiling water, become black, friable, and infusible; they are insoluble in alcohol (Pelletier, *J. Pharm.* 24, 165; *Ann. Pharm.* 29, 57). — By passing chlorine for ten minutes through a solution of 1 pt. narcotine in 400 pts. water acidulated with sulphuric-acid, an orange-yellow coloration is produced, but no turbidity (Lepage, *J. Pharm.* 26, 140). If to an aqueous narcotine-salt there is added first aqueous chlorine, then very dilute ammonia in slight excess, and lastly, carefully, drop by drop, very dilute acid, scarcely any coloration (such as would appear in presence of morphine, cinchonine, strychnine or brucine) is produced (Soubeiran & Henry, *J. Chim. méd.* 22, 134).

6. By distilling 20 grm. narcotine with concentrated aqueous *hydriodic acid*, 19 grm. iodide of methyl are obtained; that is 3 at. iodide of methyl (calcul. 21·1 grm.) from 1 at. narcotine (Matthiessen & Foster).

7. When a few drops of *oil of vitriol* are poured upon narcotine, it becomes yellow, and on heating, brown (Riegel, J. Erdmann). On adding powdered narcotine to perfectly pure oil of vitriol (free from nitric acid) covered with a few drops of water, an amber-yellow colour is produced, which passes after a few hours into orange-red (Jacquelain). If air or oxygen is allowed to have access to the colourless mixture of narcotine and oil of vitriol, it turns yellow, and afterwards red (Couerbe). According to Merck, oil of vitriol colours narcotine dirty blue, then brown-yellow; according to Schlienkamp, yellow-green; according to Serullas, Bussy, Guibourt, and Henry & Lecanu, bright yellow; it then quickly becomes orange-red, and after three days exhibits a wine-red colour. Hot oil of vitriol dissolves narcotine with effervesence and dark purple-red colour (owing to the presence of nitric acid? Kr.) (Duflos). — By heating with dilute sulphuric acid, it is converted into sulphonarcotide (Laurent & Gerhardt).

8. Cold *nitric acid* dissolves narcotine without coloration (Couerbe), on heating, it is coloured yellow (Riegel). Powdered narcotine is coloured a beautiful lemon-yellow by concentrated nitric acid, but not till after a few minutes (Merck). It is reddened by warm nitric acid, and dissolves, with formation of oxalic acid and artificial bitter (Derosne), without forming picric acid (Liebig).

Concentrated nitric acid, even in the cold, attacks it violently and converts it into a dense red resin, evolving abundance of red fumes. Acid somewhat more dilute produces a red liquid, which leaves, on evaporation, an amorphous orange-coloured residue. On boiling this residue with potash-ley, methylamine is obtained (Anderson). By slightly heating narcotine ,with concentrated nitric acid, so as to avoid the evolution of red fumes, a combustible gas, apparently nitrate of ethyl or of methyl, is evolved (Gerhardt, *Compt. Chim.* 1845, 117; *Traité*, 4, 64). — When 1 pt. narcotine, together with 2·8 pts. nitric acid of sp. gr. 1·4 and 8 pts. water (as in B. vol. xiv. p. 423), is heated uniformly to 49°, the narcotine melts to a yellowish mass, which dissolves on stirring, without evolution of red fumes, and then, when the solution is nearly complete, teropiammone (xiv. 436) is deposited, while opianyl (xiv. 422), opianic acid (xiv. 427), hemipinic acid (xiv. 430), and cotarnine (xvi, 130) remain dissolved (Anderson). On one occasion Anderson obtained also hydrate of opianyl (xiv. 424, and xvi. 134).

In this decomposition opianic acid and cotarnine must be regarded as primary, the other substances as secondary products: $C^{44}NH^{23}O^{14} + 2O = C^{20}H^{10}O^{10} + C^{24}NH^{13}O^6$. The opianyl might also be supposed to be formed by the breaking up of the narcotine: $C^{44}NH^{23}O^{14} = C^{20}H^{10}O^8 + C^{24}NH^{13}O^6$, or at the expense of the opianic acid: $2C^{20}H^{10}O^{10} = C^{20}H^{10}O^8 + C^{20}H^{10}O^{12}$. The last process, or the further oxidation of the opianic acid, yields hemipinic acid.

9. When at least twice its weight of *hyponitric acid* is poured upon 1 or 2 grm. narcotine, the mixture at once acquires a fine crimson colour, becomes hot, froths up, and gives off a large quantity of red fumes. After half a minute the action diminishes, but suddenly

becomes again more violent, so that the mass takes fire and burns with a white flame. There remains a very porous charcoal, containing picric acid in the inside. Water decolorises the red mass at first formed. (Mialhe, *J. Pharm.* 22, 583.) — According to Couerbe, nitrous oxide, nitric oxide, nitrous acid, and hyponitrous acid, have no action upon narcotine.

In contact with *oil of vitriol containing a trace of nitric acid*, narcotine takes a fine blood-red colour, and colours the acid similarly (Couerbe, Lefort); but is decolorised on addition of a little more nitric acid (Fresenius). — This behaviour was first observed by Duflos (*Schw.* 61, 217), but the coloration was ascribed by him to the action of oil of vitriol only. — A single drop of nitric acid in a pound of oil of vitriol can be thus detected. When 6 grains of narcotine is shaken with ½ an ounce oil of vitriol, containing an exceedingly small quantity of nitric acid, the mixture becomes yellow, and after 8 minutes red (Couerbe). If nitric acid is added to the mixture of narcotine and oil of vitriol, it is coloured first yellowish red, then yellowish brown (Schlienkamp, *N. Br. Arch.* 86, 279). If 7 pts. nitric acid (hyponitric acid or nitrate of potash) are mixed with 10,000 pts. oil of vitriol, the mixture becomes dark-red on addition of narcotine; the coloration is amber-yellow when oil of vitriol containing 8 pts. nitric acid to 1,000,000 is used; and even with 3 pts. nitric acid to 5,000,000 pts. sulphuric acid, the colour became darker after a few hours (Jacquelain, *N. Ann. Chim. Phys.* 7, 197; *Compt. rend.* 14, 643). Eight to twenty drops of oil of vitriol containing nitric acid (prepared by mixing 6 drops nitric acid of sp. gr. 1·25 with 100 cub. centim. water, and adding 10 drops of this mixture to 20 grm. oil of vitriol) added to narcotine, colour it onion-red, and after addition of (pure) oil of vitriol, this coloration is permanent for eight days or longer. On further adding to the mixture fragments of peroxide of manganese, it shows, after one hour, a yellow or blood-red colour, which remains unchanged, even after careful dilution with from 4 to 6 measures water, and almost complete neutralisation with ammonia; a slight excess of ammonia destroys the colour, forming an abundant dark brown precipitate, but it is reproduced on acidifying (J. Erdmann, *Ann. Pharm.* 120, 188). — In presence of nitric oxide, sulphuric acid colours narcotine pale green; if nitrous oxide is employed a fine red coloration is immediately produced (Couerbe).

Narcotine is reddened also by the following oxidising substances after addition of oil of vitriol:—*iodic acid, iodates, chloric acid, chlorate* and *perchlorate of potash, chlorous acid, chlorite of potash* and *protoxide of lead, nitrate of potash, antimoniate of potash,* and *peroxide of lead* (Lefort, *Rev. Scient.* 16, 355). On addition of peroxide of lead to the solution in sulphuric acid, it takes a dirty red colour; after a few hours it becomes purple-red and violet; on addition of *bichromate of potash* it becomes brown-green and afterwards darker (Riegel).

10. Narcotine heated with excess of dilute sulphuric acid and finely powdered *peroxide of manganese* is resolved into opianic acid (xiv. 427) and cotarnine (p. 130), with slight evolution of carbonic acid (Wöhler). On one occasion Wöhler obtained also apophyllic acid (xiii. 154), and by heating narcotine with peroxide of manganese and hydrochloric acid, or with *peroxide of lead*, hemipinic acid (xiv. 430) was also produced. — By pouring aqueous sulphate of narcotine upon peroxide of lead, heating to boiling, and adding sulphuric acid drop by drop, E. Marchand's *narcoteïne* is formed, and this, by further heating, as long as effervescence continues, is converted into opianic acid. Narcoteïne is brown, amorphous, very bitter; easily soluble in nitric acid with yellow colour, in oil of vitriol with splendid red, in water with yellow colour; the last solution is coloured red-yellow by ammonia or potash, and does not precipitate basic acetate of lead. It is very soluble in alcohol, very slightly soluble in ether (Eug. Marchand, *J. Chim. méd.* 20, 365).

11. When heated with very concentrated aqueous *potash-ley*, or with

alcoholic potash, narcotine is converted into narcotinate of potash (p. 148) (Wöhler). — Heated with excess of *potash-hydrate* to 200° or 220°, it yields methylamine or termethylamine (Wertheim). There is also produced an oily base, boiling at a much higher temperature than termethylamine (Hofmann, *Ann. Pharm.* 75, 367). Pyrrol occurs among the products of decomposition (Gr. Williams, *Chem. Gaz.* 1858, 381). — Werthem supposes the termethylamine to be the isomeric body propyla-mine; but according to Matthiessen & Foster's experiments (on the action of hydriodic acid on narcotine, p. 140), there is no doubt that it must be regarded as the former, as had been previously suggested by Hofmann (*Ann. Pharm.* 79, 29). (See also p. 138.) — 12. *Mercuroso-mercuric nitrate* colours narcotine yellow, then brown (Lassaigne, *Ann. Chim. Phys.* 45, 435).

13. Narcotine heated with excess of *bichloride of platinum* is decomposed (with formation of protochloride of platinum) into carbonic acid, cotarnine, and opianic acid, hemipinic acid being also produced by the decomposition of the opianic acid. When the smallest possible excess of bichloride of platinum is employed, narcogenine (p. 140) is formed (Blyth). For formulæ representing the decomposition, see above; they, however, still leave the formation of carbonic acid to be accounted for.

14. Narcotine does not reduce *red prussiate of potash* in alkaline solution (Kieffer, *Ann. Pharm.* 103, 277). — 15. It is not decomposed when heated for half an hour to 100° with absolute alcohol and *iodide of ethyl*, but it is partially converted into hydriodate (How).

Combinations. — *With Water.* — Narcotine does not dissolve in cold water, and is insoluble or only very slightly soluble in boiling water (Sertürner, Duflos). Narcotine (containing acid) prepared by exhausting opium with ether dissolves in 25,000 pts. water at 20°, in 7,000 pts. boiling water; narcotine free from acid, prepared by dissolving the foregoing in hydrochloric acid, precipitating with ammonia, and recrystallising from alcohol, dissolves in 1,500 pts. water at 20° and in 600 pts. boiling water (Brandes).

With Acids. — Narcotine dissolves easily in acids, combining with them to form *salts* having an acid reaction (Derosne, Sertürner). The salts are for the most part uncrystallisable, and taste more bitter than the salts of morphine; those containing weak acids are partially decomposed by a large quantity of water; those containing volatile acids are also decomposed partially by evaporation, with separation of narcotine (Derosne, Sertürner, Duflos). It is very slightly soluble in dilute acids (Merck). Caustic alkalis and alkaline carbonates and bicarbonates precipitate narcotine from solutions of its salts as a white powder insoluble in excess of the precipitant (Derosne, Sertürner), and appearing as made up of branching crystals under a magnifying power of 250 (Anderson). Alkaline bicarbonates precipitate most, but not all of the narcotine (Duflos). The presence of tartaric acid does not prevent the precipitation of narcotine-salts by alkaline bicarbonates (Oppermann, *Ann. Pharm.* 58, 48). — Phosphate of soda throws down a white powder, easily soluble in hydrochloric acid (v. Planta). Narcotine has not the power of decomposing sulphate of copper (De Vrij). — In solutions of the narcotine-salts, tincture of iodine produces a kermes-brown precipitate (v. Planta); chlorine-water a slight yellow coloration; chloride of lime a white, curdy precipitate, soluble in excess of acid with pale yellow colour; bromine-water

a white turbidity which disappears without coloration on stirring (Duflos); tincture of bromine a yellow precipitate (Merck). With oil of vitriol containing nitric acid, the salts behave like narcotine itself (p. 141) and are precipitated by basic acetate of lead (Nees v. Esenbeck). They have no action on either bromide or iodide of potassium (see below), nor on iodate, bromate, or chlorate of potash, stannic chloride, mercurous nitrate, mercuric nitrate, or nitrate of silver (Merck, Duflos). They give no blue coloration with ferric chloride. — The salts of narcotine are soluble in water, alcohol, and ether.

Carbonate of narcotine is not produced, either by treating narcotine suspended in water with *carbonic acid*, or by precipitating narcotine salts with alkaline carbonates (How, *Ann. Pharm.* 100, 375 ; *Lieb. Kopp's Jahresb.* 1854, 518).

Phosphate of Narcotine. — Turpentine-like mass, with crystals (Brandes).

Sulphate. — 100 pts. narcotine neutralise 12·5 pts. oil of vitriol (Robiquet). The uncrystallisable sulphate of narcotine contains 11·7 p. c. sulphuric acid (Brandes).

Hydriodate. — When finely powdered narcotine is heated in a sealed tube with absolute alcohol and iodide of ethyl to 100° for an hour, crystals of narcotine separate from the solution on cooling. The liquid poured off from the crystals and evaporated, after the alcohol and iodide of ethyl have been distilled off, leaves a residue which yields hydriodate of narcotine to hot water, while a small quantity of narcotine remains behind. — Separates from its solutions when evaporated spontaneously, or at 100°, as an oil, which cannot be crystallised even from alcohol or ether. Treatment with nitrate of silver and hydrochloric acid successively converts it into hydrochlorate of narcotine (How). — Iodide of potassium throws down from hydrochlorate of narcotine, a dense, white powder, which is deposited in drops after some time (v. Planta). Biniodide of potassium gives, even in very dilute solutions of narcotine, a yellowish white, permanently amorphous precipitate (Delffs, *N. Jahrb. Pharm.* 2, 31; Wagner, *Dingl.* 161, 40).

Hydrochlorate. — 100 pts. narcotine treated with dry hydrochloric acid gas at 100°, the excess of acid being afterwards displaced by dry air, is found to have absorbed 9·52 pts. hydrochloric acid (Liebig). Narcotine treated with hydrochloric acid at the common temperature, retains 13·65 p. c. hydrochloric acid in vacuo over caustic potash ; part of this escapes on heating in a stream of air, so that at 100° or 115° the product contains 8·86 p. c. (1 at. ; calculation for $C^{44}H^{23}NO^{14} = 8.83$ p. c hydrochloric acid). It dissolves in water, reacts acid, and melts with coloration when heated to 130° (Regnault). — The solution of narcotine in aqueous hydrochloric acid leaves on evaporation a transparent gum, which dissolves easily in water, and retains its hydrochloric acid, and consequent solubility in water and acid reaction, even after repeated solution and evaporation (Geiger). — The syrupy solution solidifies in the drying oven to a radiate mass, which is hard and semi-transparent when dry, and after drying at 110° contains 8·21 p. c. hydrochloric acid (Robiquet), after crystallisation from alcohol 8·02 p. c. (Regnault). (Calculation: $C^{44}H^{23}NO^{14},HCl = 8.11$ p. c. hydrochloric acid).

Narcotine produces no precipitate with *fluosilicic alcohol* (xv. 437) (Knop). — *Phosphomolybdic acid* (xiii. 164) gives with narcotine a brownish yellow, flocculent precipitate (Sonnenschein); *phosphantimonic acid* (xiv. 227) gives a yellowish white flocculent precipitate (Schulze). — Hydrochlorate of narcotine forms with *chloride of cadmium* a semi-crystalline, slightly soluble mass (Gellatly, *N. Edinb. Phil. J.* 4, 94; *Chem. Centr.* 1856, 606).

Iodide of mercury and potassium throws down from hydrochlorate of narcotine a yellowish white powder, insoluble in hydrochloric acid (v. Planta). The white precipitate (and also that produced by *bromide of mercury and potassium*) contains to 1 at. narcotine, 2 at. mercury, and 3 at. iodine or bromine; it is scarcely soluble in cold water, but dissolves in hot water and in alcohol (Groves, *Chem. Soc. Qu. J.* 11, 97).

Chloromercurate of Narcotine. — Already observed by Caillot (*Ann. Chim. Phys.* 42, 265) — Mercuric chloride throws down from alcoholic hydrochlorate of narcotine a white precipitate, which, when dissolved in a cold mixture of 2 measures of alcohol and 1 measure of fuming hydrochloric acid, with subsequent addition of water until turbidity commences, separates in small white crystals (Hinterberger, *Wien. Akad. Ber.* 7, 432; *Ann. Pharm.* 82, 311; *J. pr. Chem.* 56, 144). Not sensibly soluble in hydrochloric acid or sal-ammoniac (v. Planta).

			a.		
44	C	....	264	....	45·13
	N	....	14	....	2·39
24	H	....	24	....	4·12
14	O	....	112	....	19·11
2	Cl	....	71	....	12·13
	Hg	....	100	....	17·09

C⁴⁴NH²³O¹⁴,HCl,HgCl .... 585 .... 100·00

					Hinterberger. at 100°.
42	C	....	252	.... 44·15	.... 43·64
	N	....	14	.... 2·44	
22	H	....	22	.... 3·86	.... 3·90
14	O	....	112	.... 19·62	
2	Cl	....	71	.... 12·41	
	Hg	....	100	.... 17·52	.... 18·02

C⁴⁴NH²¹O¹⁴,HCl,HgCl .... 571 .... 100·00

a, according to Matthiessen & Foster's formula for narcotine; *b*, according to Hinterberger, who supposes the compound to contain a peculiar variety of narcotine, differing from common narcotine by containing 2 at. carbon and 2 at hydrogen less. See above, p. 138.

Hydrochlorate of narcotine throws down from *chloride of gold* a yellowish white precipitate, which turns green after a while, and is soluble in acids without coloration or reduction (Duflos). The dense, reddish-yellow precipitate does not dissolve perceptibly in hydrochloric acid (v. Planta).

Chloroplatinate of Narcotine. — To a cold dilute solution of hydrochlorate of narcotine is added just as much bichloride of platinum as is needed to precipitate it; the precipitate is collected, pressed, tritu-

rated, and washed with a very small quantity of cold water. Longer washing or heating with water would occasion partial decomposition and formation of cotarnine and opianic acid, the former of which would remain mixed with the product in the form of chloroplatinate (Blyth). — Yellow flocks, or a yellow crystalline precipitate.

Soluble in a very large quantity of hot water; the solution becomes brown by several hours' boiling, and soon afterwards deposits all the platinum, together with a small amount of organic matter, as a black precipitate : ammonia then produces in the filtrate a precipitate resembling narcotine (Anderson, *Ann. Pharm.* 96, 204). (For the decomposition with excess of bichloride of platinum, see p. 14).

Calculations.

	a.					b.		
44 C	264	....	42·61	46 C		276	....	43·57
N	14	....	2·26	N		14	....	2·21
24 H	24	....	3·87	25 H		26	....	4·10
14 O	112	....	18·08	14 O		122	....	17·69
3 Cl	106·5	....	17·19	3 Cl		105·5	....	16·81
· Pt	99	....	15·99	Pt		99	....	15·62
$C^{44}NH^{23}O^{14},HCl,PtCl^2$	619·5	....	100·00	$C^{46}NH^{25}O^{14},HCl,PtCl^2$		633·5	....	100 00

Analyses.

	Blyth. mean.		Wertheim. mean.			
				a.		b.
C	43·64	....		42·54	....	43·17
N						
H	4·23	....		4·07	...	4·15
Pt	15·80	....		15·95	....	15·72

b. is Wertheim's ethyl-narcotine. — Contains 14·58 p. c. platinum (Liebig); 15·89 p. c. (Regnault); 15·88 (How).

Bichloride of iridium and sodium precipitates from hydrochlorate of narcotine an ochre-yellow powder, soluble in hydrochloric acid (v. Planta).

Hydrosulphocyanate of Narcotine. — Acetate of narcotine gives no precipitate with sulphocyanide of potassium (Artus, *J. pr. Chem.* 8, 513); a neutral solution gives a flocculent precipitate (O. Henry, *J. Pharm.* 24, 194). The precipitate thrown down from hydrochlorate of narcotine is white or reddish, and aggregates to reddish drops (v. Planta). Appears as an amorphous powder, even under a magnifying power of 250 (Anderson, *N. J. Pharm.* 13, 443). Soluble in hot alcohol (Henry).

Acetate. — Narcotine dissolves easily in concentrated acetic acid, but not in the dilute acid, nor in water containing acetic acid. Concentrated acetic acid saturated with narcotine and evaporated in vacuo over sulphuric acid and lime, exhibits points of crystallisation after a few days, and after a month the greater part of the salt has solidified. The mother-ley is thick and can be drawn into threads; both are soluble in a small quantity of water, but the solution soon decomposes into an acid salt which remains dissolved, and soft crystals either of narcotine or of a basic salt (Berzelius, *Pogg.* 28, 441). — The solution

of narcotine in concentrated acetic acid becomes turbid on heating (Pelletier), narcotine separating even before volatilisation of acetic acid takes place (Robiquet). It is precipitated by water (Henry). When evaporated, it loses acetic acid and leaves a white, granular residue, whence water extracts a small quantity of acetate of narcotine, which loses the remainder of the acetic acid by a second evaporation (Geiger). — With 18 pts. acetate of potash dissolved in a small quantity of water, narcotine forms a solution, which is precipitated by more water (Henry).

Narcotine dissolves when heated with 5 pts. *bitartrate of ammonia* and 144 pts. water, and is not precipitated on cooling or by dilution. A solution prepared in the same way with bitartrate of potash deposits narcotine and bitartrate of potash on cooling (Henry).

Picric acid precipitates from hydrochlorate of narcotine,[s] a dense sulphur-yellow powder (v. Planta). An ethereal solution of narcotine does not precipitate alcoholic picric acid (Kemp, *Repert.* 71, 164). — The salts of narcotine are precipitated by *tannic acid* or tincture of galls, not by gallic acid (O. Henry, *J. Pharm.* 21, 212). (Comp. vii, 177). Tincture of galls causes in dilute hydrochlorate of narcotine, a turbidity which becomes a dense precipitate on addition of one drop of hydrochloric acid, and is not perceptibly soluble in more hydrochloric acid (v. Planta).

Narcotine dissolves somewhat more readily in boiling *potash-ley* than in boiling water (Brandes). It does not dissolve either in aqueous *ammonia* nor in potash-ley (Merck, Geiger).

Dissolves in 100 pts. cold and in 24 pts. boiling *alcohol*, and is precipitated therefrom by water (Derosne). Soluble in 120 pts. alcohol of 96 p. c. (Merck), in 100 pts. cold and 20 pts. boiling alcohol of 85 p. c. (Duflos). — Soluble in 126 pts. cold, and in 48 pts. boiling *ether* of sp. gr. 0·735 (Duflos); in 40 pts. boiling ether of sp. gr. 0·725 and crystallises out on cooling until 1 pt. narcotine remains dissolved in 100 pts. ether (Geiger).

Dissolves in 2·69 pts. *chloroform* (M. Pettenkofer, *N. Jahrb. Pharm.* 10, 270), in 60 pts. *acetate of ethyl*, whence it is precipitated by potash, but not by water (Henry). — Dissolves in *creosote*, even in the cold (Reichenbach), and crystallises on cooling from its solutions in warm volatile oils (Derosne). Soluble in 400 pts. *olive oil* (Pettenkofer). — More soluble in aqueous *picrotoxin* (xiv. 477) than in pure water (Pelletier & Couerbe).

Opianine.

HINTERBERGER. *Wien. Akad. Ber.* 6, 109; *Ann. Pharm.* 77, 207; *J. pr. Chem.* 53, 431. — *Wien. Akad. Ber.* 7, 432; *Ann. Pharm.* 82, 319; *J. pr. Chem.* 56, 151.

Sometimes occurs in Egyptian opium. — When this is exhausted with water for the purpose of preparing morphine, ammonia precipitates from the extract a mixture of morphine and opianine. The precipitate is washed with water and alcohol, dried, dissolved in alcohol, and the solution decolorised with animal charcoal, and allowed to crystallise, when crystals of opianine are first deposited.

Properties. Colourless, transparent, well-developed crystals of the right prismatic system. Fig. 53 without *i* and *t*. The crystals are needle-shaped, or tabular by the predominance of *t*. The octahedral faces are either only hemihedral, or, when holohedral, larger than the rest. $m : u = 116°\ 4·5'$; $u : u'$ above $= 127°\ 51'$ $a : u = 155°\ 12'$; $a : p = 114°\ 48'$; $a : a$ over $u = 130°\ 24'$; $y : y$ over $m = 87°\ 8'$; $y : y$ over $p = 92°\ 52'$. Three prisms also occur as subordinate forms: the first, between *y* and *m*, forms with *y* an angle of 175° 0'; the second likewise between *y* and *m*, makes an angle of 155° 12' with *y*; the third, between *p* and *y*, makes an angle of 96° 50' with *m* and of 173° 10' with *p*. The surfaces are for the most part plane; the prismatic faces, and sometimes also *m*, are vertically striated. Cleavage perfect parallel to *m*, imperfect parallel to *t*. Fracture conchoidal. Lustre vitreous, adamantine (Schabus, *Bestimm.* p. 76).

Opianine has no smell. In alcoholic solution it tastes strongly and persistently bitter. Reacts strongly alkaline. Exerts a narcotic action similar to that of morphine. — Unalterable at 100°.

Calculation according to		Hinterberger.		Hinterberger.
66 C	396	63·06		62·99
2 N	28	4·46		4·26
36 H	36	5·73		5·70
21 O	168	26·75		27·05
$C^{66}N^2H^{36}O^{21}$	628	100·00		100·00

By combustion with soda-lime, Hinterberger found a smaller quantity of nitrogen (2·22 p. c.), and hence gave at first the formula of opianine as $C^{66}NH^{36}O^{23}$. Anderson (*Ann. Pharm.* 98, 50) regards the proportion of nitrogen thus found as the more accurate, and in accordance therewith, calculates the formula $C^{66}NH^{37}O^{22}$ for opianine, pointing out that this base may be regarded as formed by the union of 1 at. cotarnine ($C^{26}NH^{13}O^6$) and 2 at. of the compound $C^{20}H^{12}O^8$ (Anderson's hypothetical hydride of opianyl). Comp. p. 139. — Gerhardt (*Traité*, 4, 68) and Weltzien (*Organ. Verbind.* 567) doubt the existence of opianine as distinct from narcotine.

Dissolves in *oil of vitriol containing nitric acid* with blood-red colour, which becomes light yellow by standing.—Not decomposed by *oil of vitriol;* dissolved with yellow colour by *nitric acid*.

Not soluble in *water*.

Opianine combines with *acids* to form *salts*, from the aqueous solutions of which it is precipitated by ammonia and alkalis in flocks.

Chloromercurate of Opianine. — Obtained in the same way as the corresponding narcotine-compound (p. 144). Acicular crystals, slightly soluble in water and alcohol.

				Hinterberger.
66 C	396	49·50		49·11
2 N	28	3·50		
37 H	37	4·63		4·61
21 O	168	21·00		
Hg	100	12·50		12·28
2 Cl	71	8·87		9·31
$C^{66}N^2H^{36}O^{21},HCl,HgCl$	800	100·00		

With *bichloride of platinum*, hydrochlorate of opianine forms a compound decomposable by excess of chloride of platinum

Opianine is very slightly soluble in boiling *alcohol*, and crystallises out completely on cooling.

Narcotinic Acid.

First observed by Couerbe (*Ann. Chim. Phys.* 59, 167).

Produced by heating narcotine with concentrated potash-ley, apparently with assimilation of water.

When narcotine is heated to boiling for a long time with very strong potash-ley, the mixture being frequently shaken up, there fall to the bottom oily drops of narcotinate of potash, which remain liquid after cooling, and resemble turpentine in colour and consistence. The reaction is not accompanied by evolution of ammonia. — After the ley has been poured off, the oil-drops are easily soluble in water. The yellow bitter solution becomes turbid on heating, and deposits crystalline needles of unaltered narcotine, into which the narcotinic acid is almost completely reconverted by long boiling of the greatly diluted solution, while free potash and a yellow colouring matter, probably an accidental product of decomposition, remain dissolved.

When narcotinate of potash, separated from the mother-liquor, is left to itself, it becomes opaque after a few days, owing to the separation of narcotine, and is then only partially soluble in water.

Narcotinate of potash dissolves very easily, and with yellow colour, in alcohol, remains unaltered for months in this solution, and can be obtained by evaporation as a soft amorphous mass, completely soluble in water. Mixed with water, the alcoholic solution gradually deposits crystals of narcotine, and by heating they are produced immediately. Alcoholic narcotinate of potash is also obtained by dissolving narcotine in alcoholic potash.

Hydrochloric acid throws down chloride of potassium from the alcoholic solution, while hydrochlorate of narcotine remains dissolved, and is precipitable by ammonia after dilution with water. — If excess of acetic acid is added to the alcoholic solution, the addition of ammonia causes at first no precipitate, but after a time crystals of narcotine are precipitated; they also soon separate from a solution which has been mixed with an insufficient quantity of acetic acid, and is, therefore, still alkaline. — On passing a current of carbonic acid into the alcoholic solution, a jelly, together with a large quantity of crystalline prisms, is gradually formed, and when filtered off and washed with alcohol, is resolved by water into bicarbonate of potash and narcotine. From the filtrate, which still contains a large quantity of narcotinate of potash, there gradually separate, together with a large quantity of crystals of narcotine, fine white warty crystals, which are more difficultly soluble in ether than narcotine, but are converted into narcotine on attempting to isolate them.

The aqueous solution of narcotinate of potash does not precipitate baryta- or lime-salts. With sal-ammoniac it evolves ammonia and deposits narcotine. With sugar of lead, it produces a pale yellowish precipitate (probably colourless when pure), which, in the crude state, contains 37·9 p. c. oxide of lead, and after washing yields sulphate of narcotine to dilute sulphuric acid. It dissolves in alcohol, all except a little carbonate of lead ; if the lead is precipitated from this solution by

hydrosulphuric acid, the yellow filtrate yields, on evaporation, crystals of narcotine and smaller warty crystals, which are converted into narcotine by alkalis or acids.

Narcotinate of potash gives with nitrate of silver, a pale yellow precipitate, which is easily soluble in water and does not appear in dilute solutions. Its aqueous solution soon becomes dark-coloured and afterwards black, and on heating immediately coats the glass with a blackish or copper-coloured metallic mirror, at the same time depositing crystals of narcotine.

Sulphonarcotide.

$C^{46}NH^{24}SO^{16}$ or $C^{44}NH^{22}SO^{16}$.
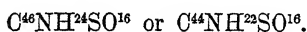
LAURENT & GERHARDT. *N. J. Pharm.* 14, 303; *N. Ann. Chim. Phys.* 24, 114; *J. pr. Chem.* 45, 371; abstr. *Compt. rend.* 27, 80; *Ann. Pharm.* 68, 360.

First observed by Duflos (*Schw.* 61, 217.)—Narcotine moistened with water dissolves when heated with a small excess of sulphuric acid; when more strongly heated, it becomes dark green and thick, without evolution of gas. On diluting with water and boiling, the resulting solution deposits sulphonarcotide on cooling as a dark-green powder, which must be washed with cold water.

		a.					*b.*			Laurent & Gerhardt.
44	C	264	....	59·45	46	C	276	....	60·26	.... 59·1
	N	14	....	3·15		N	14	....	3·06	
22	H	22	....	4·95	24	H	24	....	5·24	.... 5·3
16	O	128	....	28 83	16	O	128	...	27·95	
	S	16	....	3 62		S	16	..	3·49	... 3·6
$C^{44}NH^{22}SO^{16}$		444	....	100 00	$C^{46}NH^{24}SO^{16}$		458	...	100·00	

Laurent & Gerhardt double the formula *b.* — Sulphonarcotide is sulphate of narcotine minus 2 at. water.

When *heated* on platinum foil, it leaves a large quantity of difficultly combustible charcoal. — By *dry distillation* it yields water and a disagreeably smelling oil. — Ebullition with *nitric acid* converts it into sulphuric acid and a yellow substance soluble in ammonia. — *Ammonia* does not alter it. — It dissolves in *potash-ley* with brown colour, and is precipitable by acids in yellow flocks.

Soluble in *alcohol*, but not deposited by it in crystals.

Narcogenine.

$C^{68}N^2H^{36}O^{20} = C^{44}NH^{23}O^{14}, C^{24}NH^{13}O^6$.

BLYTH. *Ann. Pharm.* 54, 44; *Mem. Chem. Soc.* 2, 163.

Sometimes obtained as chloroplatinate, together with cotarnine, in the preparation of this base, especially when the smallest possible

excess of bichloride of platinum has been used. — Cannot be isolated, inasmuch as it breaks up into narcotine and cotarnine when separated from the platinum salt.   Blyth, who assigns to narcogenine the formula $C^{36}NH^{19}O^{10}$, views this decomposition as a process of oxidation accompanied by formation of protochloride of platinum [Blyth's formula: $2(C^{36}NH^{19}O^{10}) + 2O = C^{25}NH^{13}O^6$ (cotarnine, according to Blyth) $+ C^{46}NH^{25}O^{14} + CO^2$] ; while Laurent (*N. Ann. Chim. Phys.* 19, 370) and others regard chloroplatinate of narcogenine as a double salt containing narcotine and cotarnine.

Chloroplatinate of Narcogenine. — Long, bright orange-yellow needles. Becomes lighter coloured on addition of ammonia and, on heating, splits up completely into narcotine, which separates out, and cotarnine which, together with protochloride of platinum, remains in solution.   The mother-liquor when strongly cooled deposits a dirty white precipitate, probably Magnus's salt (vi. 304). — Ebullition with a great excess of bichloride of platinum converts it, with evolution of carbonic acid, into cotarnine, while opianic or hemipinic acid remains in solution.

			a.		
68	C		408	......	39·04
2	N		28	......	2·68
38	H		38	......	3·64
20	O		160	......	15·31
2	Pt		198	......	18·94
6	Cl		213	......	20·39

$C^{68}N^2H^{38}O^{20},2HCl,2PtCl^2$ .... 1045 .... 100·00

			b.			Blyth. *mean.*
36	C		216	....	40·33	40·62
	N		14	....	2 62	
20	H		20	....	3·73	4·11
10	O		80	....	14·95	
	Pt		99	....	18·18	18·15
3	Cl		106·5	....	19·89	

$C^{36}NH^{19}O^{10},HCl,PtCl^2$ .... 535·5 .... 100·00

Blyth gives the formula *b.*   For Wertheim's formula, see *Ann. Pharm.* 70, 71.

Appendix to Cotarnine and Narcotine.

Humopic Acid.

WÖHLER.   *Ann. Pharm.* 50, 21.

Narcotine is heated in a platinum capsule placed in an oil-bath until, at 220°, it froths up violently, evolves ammonia, and solidifies to a porous mass. This product yields to hydrochloric acid a peculiar base (p. 139), while humopic acid remains behind. The latter is dissolved in potash-ley, precipitated with hydrochloric acid, washed, dried, freed by solution in alcohol from a small quantity of a black-brown substance with which it is mixed, and lastly precipitated by water.

Dark brown, amorphous mass, resembling ferric hydrate when freshly precipitated. Dried at 120°, it contains on an average 64·20 p. c. C., 5·14 H., and 30·66 O. Wohler gives the formula $C^{48}H^{25}O^{27}$, or $C^{40}H^{19}O^{14}$.

Melts when *heated* and burns with a luminous flame, giving off the smell of opium. — When long boiled with *water* it becomes insoluble in ammonia, and then dissolves with difficulty even in potash-ley and alcohol, leaving behind a black-brown substance, probably humin.

Insoluble in *water* and dilute *acids.* — Dissolves in *alkalis* with deep saffron-yellow colour; the solutions give dark-brown gelatinous precipitates with *baryta-* and *lead-salts.* — Soluble in *alcohol,* whence it is precipitated by water.

Primary Nucleus $C^{26}H^{24}$; *Oxygen-nucleus* $C^{26}H^{12}O^{12}$.

Capsulæscic Acid.

$$C^{26}H^{12}O^{16} = C^{26}H^{12}O^{12},O^4 ?$$
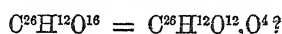
ROCHLEDER. *Wien. Akad. Ber.* 40, 37.

Occurs in the capsules of the ripe fruit of *Æsculus Hippocastanum.*

Crystals which sublime without decomposition. Isomeric with teracetogallic acid; behaves like this acid with ferric salts and reddens solution of caustic potash in the same way.

Primary Nucleus $C^{26}H^{26}$; *Oxygen-nucleus* $C^{26}H^{24}O^2$.

Oil from Oil of Cajeput:

M. SCHMIDL. *Trans. Roy. Soc. Edinb.* 22, 6, 360; *Zeitschr. Chem. Pharm.* 4, 403.

When the vapour of that portion of oil of cajeput (xiv. 510) which boils at 175° is passed over red-hot soda-lime, a yellow oil is obtained, having a different smell. The composition of that portion of this oil which boils between 180° and 185° is represented by the formula $C^{26}H^{24}O^2$.

					Schmidl. mean.
26 C	156	....	79·59	....	79·90
24 H	24	....	12·24	....	12·18
2 O	16	....	8·17	....	7·92
$C^{26}H^{24}O^2$	196	....	100 00	....	100·00

Convolvulinolic Acid.

$$C^{26}H^{24}O^6 = C^{26}H^{24}O^2,O^4.$$
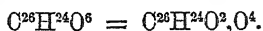
W. MAYER. *Ann. Pharm.* 83, 132; further 95, 164; announcement of the results 92, 125.

Identical with *Rhodeoretinolic acid* so far as its salts are treated of in Mayer's first memoir; but Mayer's free rhodeoretinolic acid (*Ann. Phorm.* 84, 133) is the same as the convolvulinol of his later memoirs.

Formation and Preparation. See below, p. 154. Convolvulinolate of baryta is prepared by dissolving convolvulinol in baryta-water (ammonia or solution of potash) and this salt is decomposed with hydrochloric acid.

Properties. A crystalline mass resembling convolvulinol. Melts between 42° and 42°·5, solidifies at 36° ; reacts strongly acid.

						Mayer.
26 C	.....	156	.....	68·42	.....	68·53
24 H	.....	24	.....	10·53	.....	10·76
6 O	.....	48	.....	21·05	.....	20·71
C²⁶H²⁴O⁶	.....	228	.....	100·00	.....	100·00

Nitric acid attacks it violently, and converts it into ipomæic (xiv, 494) and oxalic acids. $C^{26}H^{24}O^6 + 6(NO^5,HO) = C^{20}H^{18}O^8 + 2C^2HO^4 + 10HO + 2CO^2 + 6NO^2.$

Combinations. Convolvulinolic acid combines with *bases* forming salts, which can also be obtained by the action of caustic or carbonated alkalis or alkaline earths on convolvulinol. They contain $C^{26}H^{23}MO^6$: Mayer's earlier formula was $C^{36}H^{33}MO^{10}$. The salts of the alkalis are easily soluble in water and alcohol, those of the alkaline earths more difficultly.

Convolvulinolate of Baryta. — Hot alcoholic convolvulinol (or alcoholic convolvulinolic acid) is poured into an excess of warm barytawater; the mixture is boiled for a few minutes, and filtered boiling hot; and the needles which separate on cooling are recrystallised from aqueous alcohol. — Fine, colourless needles, grouped in stars, and melting to an oil without losing water. — More easily soluble in water than jalappinolate of baryta.

		at 100°.			Mayer.
26 C	.....	156	....	51·23	....	51·15
24 H	.....	24	....	7·88	....	8·25
6 O	.....	48	....	15·77	....	15·12
BaO	.....	76·5	....	25·12	....	25·18
C²⁶H²³BaO⁶ + HO	.....	304·5	....	100·00	....	100 00

Mayer formerly examined a baryta-salt containing free convolvulinolic acid as an admixture.

Convolvulinolate of Lead. — Obtained as a white precipitate, which dries up over oil of vitriol to a yellowish mass resembling honey, by precipitating convolvulinolate ·of ammonia with sugar of lead. — Very slightly soluble in water, rather more easily soluble in alcohol.

					Mayer. *mean.*
C²⁶H²³O⁵	.....	219	....	66·16	
PbO	.....	112	....	33·84	.... 33·85
C²⁶H²³PbO⁵	.....	331	....	100·00	

Convolvulinolate of Copper. — The aqueous ammonia-salt is precipitated with acetate of copper, to which a small quantity of acetic acid has been added, and the precipitate is dried at 100°. — Blue-green; fusible at 110° to a clear liquid, which solidifies to a highly lustrous, splendid dark green, amorphous mass. — Insoluble in water, scarcely soluble in alcohol.

		at 100°.				Mayer.
26	C	156	....	58·21	....	58·26
24	H	24	....	8·93	....	8·98
6	O	48	....	17·96	....	18·23
	CuO	39·6	....	14·90	....	14·53
$C^{26}H^{23}CuO^6 + HO$	....	267·6	....	100·00	....	100·00

Mayer previously examined a salt precipitated without addition of acetic acid, and containing more oxide of copper.

Convolvulinolate of Silver. — Obtained in white flocks, which blacken easily in the light, by precipitating the ammonia-salt with nitrate of silver. — Insoluble in water; difficultly soluble in alcohol.

Convolvulinol.

$$C^{26}H^{25}O^7 = C^{26}H^{24}O^6, HO ?$$
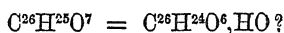
G. A. KAYSER. *Ann. Pharm.* 51, 97.
W. MAYER. *Ann. Pharm.* 83, 132; further 95, 164; announcement of the results, 92, 125.

Rhodeoretinol, Rhodeoretinolic acid. Formerly Mayer did not distinguish between the neutral convolvulinol and the convolvulinolic acid produced from it.

Formation. Convolvulin and convolvulic acid break up by prolonged contact with hydrochloric or dilute sulphuric acid at a high temperature, into sugar and convolvulinol (Kayser). Convolvulic acid undergoes the same decomposition in contact with emulsin between 35° and 40°. $C^{62}H^{53}O^{35} + 8HO = C^{26}H^{25}O^7 + 3C^{12}H^{12}O^{12}$ (Mayer).

Preparation. A moderately concentrated aqueous solution of convolvulic acid is mixed with half its bulk of fuming hydrochloric acid, and left to itself for 6 or 8 days, or until it solidifies to a magma of crystals; this is placed on a filter, and purified by washing with cold water, fusion under hot water, and recrystallisation from alcohol or ether (Mayer). It is obtained in a state of less purity by passing hydrochloric acid into alcoholic convolvulin (Kayser), or by boiling convolvulic acid with dilute sulphuric acid (Mayer): by the former process it is obtained as an oil.

Properties. Dazzling white, very long, thin and pliable needles, which melt at 38·5° or 39°, and solidify to a crystalline mass at 36°. It has a slight acid reaction. Has no smell; tastes bitter and irritating. When melted with water it gives off the smell of St. John's bread (Mayer).

at 100°.				Kayser.		Mayer. *mean.*
26 C	156	....	65·82	....	66·38	.... 65·66
25 H	25	....	10·55	....	10 67	.... 10·72
7 O	56	....	23·63	....	22 95	.... 23·62
$C^{26}H^{25}O^{7}$	237	....	100·00	....	100 00	.... 100·00

Earlier formulæ: $C^{30}H^{23}O$ (Kayser), $C^{36}H^{34}O^{10}$ (Mayer). Kayser examined coloured oily convolvulinol.

Decompositions. 1. Volatilises when *heated* on platinum-foil, apparently without decomposition, giving off an irritating smell which excites coughing, and leaving a residue of charcoal. — 2. *Burns* with a bright flame. — 3. *Oil of vitriol* colours it yellowish at first, then amaranth-red (Mayer); cold oil of vitriol does not alter it (Kayser). — 4. In contact with aqueous *alkalis*, or *alkaline earths*, it loses 1 at. water, and is converted into convolvulinolic acid (Mayer). $C^{26}H^{25}O^{7}$ + BaO,HO = $C^{26}H^{23}BaO^{6}$ + 3HO. According to Kayser it is not altered by boiling potash-ley. — 5. *Nitric acid* converts it into ipomæic (xiv. 494) and oxalic acids (Mayer).

Combinations. Dissolves with difficulty in pure *water*, somewhat more easily in acidulated water, and crystallises by slow cooling of very dilute solutions. — Very soluble in *alcohol*, less so in *ether*, and crystallises by slow evaporation (Mayer).

Conjugated Compounds of Convolvulinolic Acid or of Convolvulinol.

Convolvulin.

$$C^{62}H^{50}O^{32} = C^{26}H^{20}O^{2},3C^{12}H^{10}O^{10}.$$
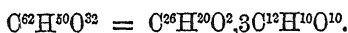
KAYSER (1844). *Ann. Pharm.* 51, 81.
W. MAYER. *Ann. Pharm.* 83, 121; abstr. *J. pr. Chem.* 57, 454; *N. Ann. Chim. Phys.* 36, 495; *Chem. Gaz.* 1853, 21. — *Ann. Pharm.* 92, 125; in detail *Ann. Pharm.* 95, 161; abstr. *J. pr. Chem.* 67, 267; *N. Ann. Chim. Phys.* 45, 494.

Comp. xv. 342. *Rhodeoretin.* — The chief (and in ether insoluble) constituent of the resin of the tuberose jalap-root of *Ipomœa Purga* (*Handbuch* viii. *Phytochem.* 60), different from Marquardt's *convolvulin*. — On the preparation of jalap-resin, see Wolf (*Repert.* 29, 372), Planche (*Bull. Pharm.* 6, 26), Geiseler (*N. Br. Arch.* 13, 221), Nativelle (*N. J. Pharm.* 1, 228), Soubeiran (*N. J. Pharm.* 10, 195). On the adulteration of jalap-resin, see Blanche (*Ann. Pharm.* 16, 87), John (*Ann. Pharm.* 28, 94), Gobley (*N. J. Pharm.* 3, 461), Vee & Poulens (*N. J. Pharm.* 12, 119); on the modes of distinguishing it from the resin of larch-fungus, see Trommsdorff (*N. Tr.* 25, 1, 203), from the resin of jalap-stems, Hanle (*Repert.* 48, 365). On its solubility in alcohol, see Flückiger (*Pharm. Viertelj.* 11, 61). See further on jalap-resin: Cadet de Gassicourt (*Repert.* 6, 24; *J. Pharm.* 3, 495), Martius (*Kastn. Arch.* 6, 382), Meylink (*Repert.* 32, 443), Nees v. Esenbeck & Marquardt (*Ann. Pharm.* 10, 122), Funcke (*Br. Arch.* 20, 256), Gerber (*Br. Arch.* 21, 202). — Buchner & Herberger attributed basic properties to the active constituent of jalap-resin and designated it *Jalappin.* According to Sandrock (*N. Br. Arch.* 64, 160), the portion of jalap-resin which is insoluble in ether consists of two distinct resins, one of which (*alpha-resin*) is precipitable by alcoholic sugar of lead, while

the other (*beta-resin*), not precipitable by sugar of lead, is converted by alkalis into his (Sandrock's) ipomœic acid (precipitable by basic acetate of lead from the neutral potash-salt) and jalappic acid. Kayser's rhodeoretin (the convolvuln of this Handbook) is, according to Sandrock, a mixture of alpha- and beta-resins, and Buchner & Herberger's jalappin is identical with beta-resin. Mayer showed, on the contrary, that Sandrock's two resins and acids do not differ essentially from each other, and are the same as convolvulin and convolvulic acid.

Preparation. Jalap-root is exhausted with boiling water, then dried and pulverised; and the powder is extracted three times with twice its weight of alcohol of 90 p.c. Water is added to the whole quantity of tincture so obtained until turbidity begins; and the liquid is boiled twice with bone-charcoal, then filtered and evaporated, whereby a yellow, brittle resin is obtained. This is pulverised, extracted four or five times with ether, then dissolved three times successively in the smallest possible quantity of absolute alcohol, and precipitated by ether (Mayer). Kayser operates similarly, but instead of boiling out the root with water, he boils the resin obtained by means of alcohol of 80 p.c., and washes with ether, as well as precipitates the alcoholic solution by ether, less frequently. — In order to prepare their jalappin, Buchner & Herberger dissolve jalap-resin in alcohol, precipitate with acetate of lead, and mix the filtrate with ammonia and water. They also redissolve the last precipitate in alcohol, digest with very dilute sulphuric acid, remove the sulphuric acid by means of hydrate of lead, evaporate, and exhaust the residue with alcohol.

Properties. Colourless mass, transparent in thin layers: brittle at 100°, and yields a white powder. If it contains a small quantity of water, it becomes soft even below 100° and can be drawn out to threads having a mother-o'-pearl lustre (Mayer). Becomes soft at 141°, melts at 150° without losing water to a clear, yellowish liquid (Kayser, Mayer). Without taste or smell. Reacts slightly acid in an alcoholic solution. Has a purgative action.

					Kayser. *mean.*		Mayer. *mean.*
62	C	372	....	54·87	.... 55·96	....	54·79
50	H	50	....	7·37	.... 7·91	....	7·96
32	O	256	....	37·76	...... 36·13	....	37·25
	$C^{62}H^{50}O^{32}$	678	....	100·00	.... 100·00	....	100 00

$C^{12}H^{35}O^{10}$ according to Kayser, $C^{72}H^{50}O^{36}$ Mayer's earlier formula. Differs from jalappin by containing $3C^2H^2$ less. — On the formulæ of convolvulin and its derivatives, see also Laurent (*Compt. rend.* 35, 379).

Decompositions. 1. Begins to decompose when *heated* above 155°; turns brown when more strongly heated on platinum-foil; *burns* with a bright smoky flame, giving off an empyreumatic smell and a smell of caramel, and leaves a shining charcoal. — 2. When covered with *oil of vitriol*, it dissolves after about ten minutes with fine carmine-red colour (Kayser), amaranth-red (Mayer), and after a few hours deposits a brown resin. Water throws a brown oil from the red solution, while sugar remains dissolved (Mayer). — 3. When *hydrochloric acid* is passed into its alcoholic solution, convolvulin breaks up, on leaving the solution to itself, into convolvulinol and sugar, the former of which is precipitated as an oil on addition of water to the dark red-yellow solution $C^{62}H^{50}O^{32}$ + $11HO = C^{26}H^{26}O^7 + 3C^{12}H^{12}O^{12}$ (Mayer). — 4. Dissolves without alteration in cold concentrated *nitric acid* and is precipitated by ammonia; it dis-

solves in warm dilute nitric acid with decomposition (Kayser). Concentrated *nitric acid* causes violent evolution of nitric oxide gas and converts it into oxalic acid and ipomæic acid (xiv. 494) (Mayer). — 5. Convolvulin dissolves in aqueous *alkalis* and *alkaline earths* (taking up 3 at. water and forming a convolvulinate : *Kayser, Mayer*) and cannot then be reprecipitated by acids (Cadet de Gassicourt, Trommsdorff). Strong aqueous ammonia produces the same effect after digesting for some time (Kayser). Aqueous alkaline carbonates dissolve convolvulin but slightly in the cold, more easily on boiling, likewise producing convolvulic acid (Kayser); its formation takes place slowly, however, so that water still causes a precipitate of convolvulin after half-an-hour's boiling (Mayer). Even after long boiling of a solution of convolvulin in potash-ley, the addition of acids or of water sometimes throws down unaltered convolvulin (Sandrock).

Convolvulin dissolves very slightly in *water* (Mayer). It dissolves easily in *acetic acid* (Buchner & Herberger, and others), in all proportions in *alcohol*, but not in *ether*. The portion of jalap-resin which is insoluble in ether does not dissolve in *volatile* or *fat oils* (Cadet de Gassicourt) ; it dissolves easily in *acetic ether* at 45°—50°; it dissolves with tolerable ease in *oil of turpentine* and is precipitable by water (Martius). It does not dissolve in oil of turpentine at 60° (Jahn, *Ann. Pharm.* 28, 95).

Convolvulic Acid.

$$C^{62}H^{53}O^{35}.$$
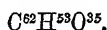
G. A. KAYSER. *Ann. Pharm.* 51, 85.
W. MAYER. *Ann. Pharm.* 83, 143 ; further 92, 125, and 91, 161.

Hydrorhodeoretin (Kayser). *Rhodeoretic acid* (Mayer). — Respecting Sandrock's statements (*N. Br. Arch.* 64, 160), see under Convolvulin (p. 154).

Formation. Convolvulin treated with aqueous ammonia, potash, or soda, or with baryta-water, takes up water and is converted into convolvulic acid (Kayser). $C^{62}H^{50}O^{32} + 3HO = C^{62}H^{58}O^{35}$ (Mayer).

Preparation. 100 grammes of convolvulin are heated to boiling with 1lb. of baryta-water, the liquid being kept stirred ; the baryta is removed from the clear cooled solution by means of a slight excess of sulphuric acid; the turbid mixture is shaken up with levigated carbonate of lead and filtered; the dissolved lead is removed by hydrosulphuric acid; and the colourless filtrate is evaporated on the water-bath (Mayer). — Kayser digests convolvulin with strong aqueous ammonia until it is dissolved, evaporates the excess of ammonia, precipitates the aqueous solution with basic acetate of lead, decomposes the washed lead-salt under water by hydrosulphuric acid, and evaporates the filtrate.

Properties. Amorphous, white, very hygroscopic mass, which becomes soft above 100°, melts between 100° and 120° and reacts strongly acid. By itself, it has no smell ; when dissolved in water it has a faint smell of quinces (Mayer). Has a purely bitter taste (Kayser).

	at 100°—120°.			Kayser. *mean.*		Mayer. *mean.*
62 C 372		....	52·70	.... 54·72	....	52·60
53 H 53		....	7·52	.... 8·33	....	7·92
35 O 280		....	39·78	.... 36·95	....	39·48
$C^{62}H^{53}O^{35}$ 705		....	100·00	.... 100·00	....	100·00

Kayser examined a brownish coloured, imperfectly pure acid. He formerly gave the formula $C^{42}H^{36}O^{21}$, and Mayer $C^{72}H^{64}O^{40}$.

Decompositions. 1. Decomposes at 120°, and *burns* when heated on platinum-foil with a bright smoky flame and gives off a smell of caramel. — 2. By ebullition with dilute *sulphuric acid,* or when its aqueous solution is mixed with concentrated *hydrochloric acid* and left to stand, it breaks up into convolvulinol (p. 153) and sugar (Mayer.) — 3. With *oil of vitriol,* it behaves like convolvulin. — 4. *Nitric acid* of sp. gr. 1·3 attacks it violently at the common temperature after being in contact for some time, evolves red fumes, and converts it into oxalic and ipomæic (xiv. 494) acids. Nitric acid of sp. gr. 1·18 forms, after 12 hours, sugar and convolvulinol. — It is decomposed by *emulsin* at common temperatures in the same way as by dilute acids (Mayer).

Combinations. Convolvulic acid dissolves in *water* in all proportions. — With *bases* it forms the convolvulinates. These salts are amorphous, easily soluble in water and alcohol; they smell of quinces when dissolved in water, melt when heated, and burn with a luminous smoky flame, and an empyreumatic smell like that of caramel. — Aqueous convolvulic acid and convolvulate of ammonia do not precipitate neutral metallic salts, but produce dense white flocks in basic acetate of lead. Aqueous convolvulic acid displaces carbonic acid, especially on boiling, from the carbonates of the alkalis and alkaline earths and from carbonate of lead.

Convolvulate of Potash. — The aqueous acid is neutralised with carbonate of potash, the solution is evaporated to dryness, and the residue exhausted with alcohol. — Amorphous, pale yellow mass. Dissolved in water it smells of quinces, has a bitter taste, and melts between 100° and 110°. — Dissolves easily in water, with difficulty in alcohol (Mayer).

			Mayer.
62 C 372	....	50 05	.... 50·48
52 H 52	....	6·98	.... 7·55
34 O 272	....	36·62	.... 36·31
KO .... 47·2	....	6·35	.... 5·66
$C^{62}H^{52}KO^{35}$ .... 743·2	....	100 00	.... 100·00

Convolvulate of Potash with Convolvulin? — Convolvulin dissolves with yellow colour in boiling aqueous carbonate of potash. On evaporating to dryness, taking up the residue with absolute alcohol, and again evaporating, a yellowish white salt is obtained, which is neutral, melts at 105°, and dissolves easily in water and alcohol (Kayser). Even after half-an-hour's boiling of the solution of convolvulin in carbonate of potash, water throws down convolvulin from it: hence this substance remains mixed or combined with the convolvulate of potash so prepared (Mayer).

Calculation according to Mayer.   Kayser.
                                                     mean.

124	C	744	....	52·35	....	52·98
102	H	102	....	7·17	....	7·57
66	O	528	....	37·18	....	36·14
	KO	47·2	....	3·30	....	3·31

$C^{62}H^{52}KO^{35} + C^{62}H^{50}O^{32}$ .... 1421·2 .... 100·00 .... 100·00

Convolvulate of Baryta. — a. *Normal.* — 1. Baryta-water is added
to aqueous convolvulic acid until a faint alkaline reaction is produced;
the liquid is warmed till the excess of baryta separates as carbonate,
and the neutral filtrate is evaporated to dryness (Kayser). — 2. An
excess of convolvulin is boiled with baryta-water; the liquid is filtered;
baryta-water is added to the filtrate until it reacts slightly alkaline;
carbonic acid is passed through it; and it is then warmed, filtered a
second time, and evaporated (Mayer). — Amorphous, white powder,
fusible at about 105°, easily soluble in water and alcohol, but (when pre-
pared according to method 1) it is precipitable from its aqueous solu-
tion by absolute alcohol. — Prepared by method 2, it perhaps contains unaltered
convolvulin (Mayer).

Calculation according to Mayer.   Kayser.   Mayer.
                                               mean.

62	C	372	....	48·15	....	50·65	....	48·85
52	H	52	....	6·73	....	7·54	....	7·25
34	O	272	....	35·35	....	34·18	....	35·16
	BaO	76·5	....	9·77	....	7·63	....	8·74

$C^{62}H^{52}BaO^{35}$ .... 772·5 .... 100·00 .... 100·00 .... 100·00

b. *Four-sevenths Convolvulate?* — By boiling convolvulin with excess
of baryta-water, passing carbonic acid through the hot solution, and
evaporating the filtrate on the water-bath, a salt similar to the normal
salt is obtained (Mayer).

Calculation according to Mayer.   Mayer.
                                                     at 100°. *mean.*

248	C	1488	....	45·19	....	45·42
205	H	205	....	6·22	....	6·80
133	O	1064	....	32·33	....	31·68
7	BaO	535·5	....	16·26	....	16·10

$3C^{62}H^{51}Ba^{2}O^{35} + C^{62}H^{52}BaO^{35}$ .... 3292·5 .... 100·00 .... 100·00

Convolvulate of Lime. — Obtained by boiling convolvulic acid with
milk of lime, passing carbonic acid into the hot filtrate, filtering again,
and evaporating. — An amorphous, slightly yellow mass. Contains
6·00 p. c. lime (Sandrock), 6·19 p. c. (Mayer).

Convolvulate of Lead. — *One-third.* — The aqueous acid, or ammonia-
salt, gives no precipitate with acetate of lead by itself, but does so
on addition of ammonia. With basic acetate of lead dense white
flocks are produced. — Somewhat soluble in water (Kayser).

Calculation according to Mayer. Kayser.
mean.

62	C	...	192	...	36·61	...	36 81
50	H	...	50	...	4·92	...	5·33
32	O	...	256	...	25·23	...	25·15
3	PbO	...	336	...	33·24	...	32·71

$$C^{62}H^{50}Pb^3O^{35} .... 834 .... 100·00 .... 100·00$$

Convolvulate of Silver. — When the aqueous baryta-salt is precipitated with sulphate of silver, the filtrate containing silver decomposes by evaporation on the water-bath (Kayser).

Convolvulic acid dissolves in *alcohol* in all proportions; it does not dissolve in *ether.*

Appendix to Convolvulin.

Portion of the resin of tuberose jalap-root which is soluble in ether. Sandrock's *Gamma-resin.* — The ethereal solutions obtained in the preparation of convolvulin (p. 155) are evaporated; the residue is twice dissolved in alcohol, and precipitated with water (Kayser). Sandrock evaporates only the ethereal solution. See also Boullier (*J. Chim. méd.* 14, 326).

According to Kayser, it is a brownish oil which makes greasy stains on paper, and, if left to itself, remains soft and sticky for several months, but in contact with water, solidifies partially to crystalline needles. — According to Sandrock, a tough, soft, yellow resin, which does not harden by exposure to air, or at 100°. Has an irritating taste, smells like jalap-root, very strongly and disagreeably (Kayser). Reddens litmus strongly. — Volatilises when *heated* on platinum-foil, and *burns* when set on fire with a bright flame, and a sharp unpleasant smell (Kayser). — With *oil of vitriol* it forms a solution which is red at first, and afterwards purple (Sandrock). — Does not dissolve in *hydrochloric, nitric,* or *acetic acid,* even on heating (Kayser). According to Sandrock it dissolves in acetic acid. — Dissolves easily in aqueous *alkalis,* and is precipitated by acids unaltered (Kayser); in flocks after long boiling, and by sulphuric acid as a jelly. (Sandrock). In alcoholic solution it gives a yellow precipitate with alcoholic *sugar of lead* (Kayser), a white precipitate (Sandrock). — Dissolves completely in *amylic aldehyde* (xi. 17) (Trautwein).

The *acid produced by boiling the resin with soda-ley* dissolves but slightly in pure water, easily in water containing ammonia. It forms a yellowish potash-salt, which crystallises from alcohol in granules, and precipitates a white powder when its solution is mixed with sugar of lead. On decomposing this lead-salt by hydrosulphuric acid, the acid remains behind with the sulphide of lead, and can then be extracted by ammonia or alcohol (Sandrock).

Oxygen-nucleus $C^{26}H^{18}O^8$.

Syringenin.

$$C^{26}H^{18}O^{10} = C^{26}H^{18}O^8,O^2 ?$$
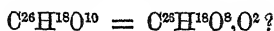
KROMAYER. *N. Br. Arch.* 109, 23. — *Epistolary Communication.*

Formation. By boiling syringin with dilute hydrochloric acid, syringenin and sugar are obtained. $C^{38}H^{26}O^{20} + 2HO = C^{26}H^{18}O^{10} + C^{12}H^{12}O^{12}$.

Aqueous syringin is warmed in the water-bath with dilute hydrochloric acid (sulphuric acid causes further alteration) for five minutes, or until the liquid, which is milky and turbid at first, has become clear by deposition of viscid grey-blue flocks. These solidify on cooling to a hard mass, which, after removal of the acid liquid, is covered with water, whereby it becomes bright pink.

Obtained as an amorphous, bright pink mass, easily reduced to a granular powder, and containing a variable proportion of water, which it gives off at 100°. Between 170° and 180° it melts to a brown tough mass. Permanent in the air. Tasteless. Neutral.

		at 100°.			Kromayer.
26 C	....	156	....	61·41	.... 61·40
18 H	....	18	....	7·09	.. .. 6·94
10 O	....	80	....	31·50	.. .. 31·66
$C^{26}H^{18}O^{10}$	....	254	....	100·00	.... 100·00

Burns when heated above its melting point. — With *oil of vitriol* and *nitric acid*, it behaves like syringin (p. 162). — Fuming *hydrochloric acid* colours alcoholic syringenin a fine dark blue, becoming violet when boiled. — It reduces silver from the *ammonio-nitrate* on boiling.

Combinations. — With *Water.* — Air-dried syringenin loses 7·05 p. c. water at 100°, then nothing more at 115° (Calculation 2 at. = 6·61 p. c. water); but a specimen obtained from the alcoholic solution by spontaneous evaporation, lost 10·04 p. c. water at 100°.

Syringenin is insoluble in *water*.

It dissolves with yellowish colour in aqueous *ammonia* and *potash*, and is precipitated by acids in light rose-coloured flocks. — It is precipitated as a dirty white jelly by an alcoholic solution of *basic acetate of lead;* not altered by *sesquichloride of iron.*

It dissolves in *alcohol* with light cherry-red colour, is precipitated by water, and remains as a light cinnamon-coloured powder when the solution is left to evaporate. Insoluble in *ether.*

Appendix to Syringenin.

Syringopicrin.

KROMAYER. *N. Br. Arch.* 102, 26. — *Epistolary Communication.*

Remains in the mother-liquor obtained in the preparation of syringin, as described on the following page, and is separated therefrom by means of animal charcoal. The charcoal is then washed with warm water and boiled with alcohol, which dissolves out the syringopicrin, and leaves it on evaporation in the form of a brown syrup. It is purified by solution in alcohol and decoloration with animal charcoal. The solution is then evaporated and the residue

treated with ether, which takes up a substance having an irritating taste, and leaves syringopicrin undissolved.

Faintly yellow transparent mass, which may be rubbed to a white powder permanent in the air. Melts below 100°, and solidifies to a brittle mass on cooling. Has a strong bitter taste, and slight acid reaction. — Contains 49·08 p. c. C., 7·67 H. and 43·25 O., agreeing with the formula $C^{26}H^{24}O^{17}$ (calc. 49·37 C., 7·59 H. and 43·04 O.), and is, therefore, produced from syringenin by assumption of 6 at. HO. and 1 at. O.

Burns away completely when strongly heated. — Dissolves in *oil of vitriol* with greenish colour passing into brown. — When boiled with *dilute sulphuric acid*, it gives off a peculiar odour, and then reduces an alkaline solution of cupric oxide. — Unaltered syringopicrin boiled with an alkaline solution of cupric oxide colours it green without separating cuprous oxide. — From an *ammoniacal silver solution* at the boiling heat, it reduces the metal.

Dissolves easily in *water.* — It is not altered or precipitated by aqueous *alkalis, ferric chloride* or *basic acetate of lead.*

Conjugated Compound of Syringenin.

Syringin.

$$C^{38}H^{28}O^{20} = C^{26}H^{18}O^{10}, C^{12}H^{10}O^{10}.$$

BERNAYS (1841). *Repert.* 74, 348; *J. pr. Chem.* 25, 121.
MEILLET. *N. J. Pharm.* 1, 25; *J. pr. Chem.* 26, 316; *Ann. Pharm.* 40, 319.
KROMAYER. *N. Br. Arch.* 108, 7; 109, 18; *Chem. Centr.* 1862, 193. — *Epistolary Communication.*

Discovered by Bernays, investigated chiefly by Kromayer. Braconnot (*Ann. Chim.* 70, 283) described a syringa-bitter, precipitable by basic acetate of lead, which however had nothing in common with syringin. Meillet described, under the name of *Lilacin,* a crystallisable bitter principle of syringa, which he obtained by boiling the green seed-capsules, precipitating the decoction with neutral acetate of lead, evaporating the filtrate, with addition of calcined magnesia, treating the residue with water to remove acetate of magnesia and mannite, and then boiling it with alcohol. The relations of this lilacin to syringin, from which it differs by its pure bitter taste and insolubility in water, have not been exactly determined. Erdmann (*J. pr. Chem.* 26, 317) did not succeed, by following either Bernays' or Meillet's directions, in obtaining the bodies described by them, perhaps because he collected the material in April. Ludwig (*N. Br. Arch.* 91, 289) regards Bernays' syringin as a mixture of lilacin with mannite (xv. 357); but even if it did contain mannite, it exhibited, with oil of vitriol, the same reaction as (Kromayer's) syringin.

Occurrence. In the bark of the lilac, more abundantly in March than in April, not in the leaves or in the half-ripe fruit, and only in traces in the leaf-buds. It disappears in the course of vegetation, its place being apparently supplied by syringopicrin (Kromayer). — The bark of privet (*Ligustrum vulgare*) contains a substance perhaps identical with syringin (Reinsch, *Jahrb. pr. Pharm.* 16, 393). See xv. 357, and below.

Preparation. The bark is exhausted with boiling water; the extract precipitated with basic acetate of lead; the filtrate treated with

hydrosulphuric acid, and after removal of the sulphide of lead, evaporated to a thin syrup, which solidifies in the course of a day to a crystalline pulp. This mass is purified by stirring it up with cold water, then pressing, and recrystallising it from boiling water, with aid of animal charcoal. The syringin dissolved in the wash-waters is obtained by evaporating the liquid, and agitating the residue with alcohol, which takes up the syringin (Bernays, Kromayer).

Properties. The hydrated crystals (see below) give off their water and become opaque at 115°, and the anhydrous syringin melts at 212° to a colourless liquid, which solidifies on cooling to an amorphous, transparent, hard, friable mass.—Tasteless. Neutral. (Kromayer).

		at 115°.			Kromayer.
38 C	......	228	......	54·81	...... 51·51
28 H	......	28	......	6·73	...... 6·95
20 O	......	160	..	38·46	... 38·54
$C^{38}H^{28}O^{20}$	......	416	......	100·00	...... 100·00

Decompositions. 1. Syringin when *heated* decomposes below its melting point, giving off an odour of caramel and burning away. — 2. The aqueous or alcoholic solution of syringin acquires a fine dark blue colour when mixed with an equal volume of *oil of vitriol;* with a larger quantity of oil of vitriol the colour changes to a beautiful violet, and the liquid on standing deposits blue, and on addition of water, grey-blue flocks, which dissolve with cherry-red colour in alcohol and in ammonia. — 3. When cautiously heated with fuming hydrochloric acid, it dissolves without coloration, but on boiling, the solution assumes a light violet-red colour and deposits blue flocks. — 4. An aqueous solution of syringin through which *chlorine gas* is passed acquires a red-brown colour, but after a while becomes quite colourless. At the same time an acid is formed, having a bitter, irritating taste, and assuming a dark-blue colour when mixed with sesquichloride of iron. — 5. Syringin dissolves quickly in strong *nitric acid*, forming a deep blood-red solution.

6. When aqueous syringin is heated with dilute *hydrochloric acid,* the solution becomes milky and deposits adhering lumps of syringenin, whilst fermentable sugar remains dissolved:

$$C^{38}H^{28}O^{20} + 2HO = C^{26}H^{18}O^{10} + C^{12}H^{12}O^{12}.$$
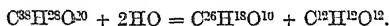
100 pts. crystallised syringin yielded 61·77 pts. air-dry syringenin and (38·45 to 43·5 pts.) on the average 41 pts. sugar (calc. 62·67 pts. hydrate of syringenin and 41·47 sugar : Kromayer).

Syringin does not reduce either *cuprate of potash* or *nitrate of silver,* and is not altered by *alkalis* (Kromayer).

Combinations. — *With Water.* — *Crystallised Syringin.* Long, colourless, transparent needles, which give off 4·5 p. c. water at 115°. (2 at. = 4·33 p. c. HO) (Kromayer).

		at 100°.			Kromayer.
38 C	......	228	....	52·53	.... 52·31
30 H	......	30	....	6·91	.... 7·34
22 O	......	176	....	40·56	.... 40·35
$C^{38}H^{28}O^{20},2Aq.$	......	434	....	100·00	.... 100·00

Syringin dissolves sparingly in cold, easily in hot *water*. It does not precipitate *metallic salts.* — It is soluble in *alcohol*, not in *ether* (Kromayer, Bernays).

Appendix to Syringin.

Ligustrin.

POLEX. *N. Br. Arch.* 17, 75.
KROMAYER. *N. Br. Arch.* 105, 9. — *Die Bitterstoffe*, Erlangen, 1862, 56.

Not known in the perfectly pure state. — Occurs in the bark of privet (*Ligustrum vulgare*) (Polex). The bark collected in spring contains ligustrin and a substance resembling syringopicrin (p. 160); the leaves contain only the latter, together with mannite (Kromayer).

The dry comminuted bark is boiled with alcohol; the extracts mixed with water, and the alcohol completely distilled off; the residue is set aside for 24 hours to deposit resin and chlorophyll; the liquid is strained, set to ferment with yeast, digested with milk of lime after the fermentation is ended, to precipitate magnesia-salts, — then filtered, exactly neutralised with dilute sulphuric acid, and concentrated; and the gypsum which separates after a few days is removed. The remainder of the lime is precipitated by oxalic acid; the filtered solution precipitated with basic acetate of lead; the liquid again filtered; hydrosulphuric acid passed into the filtrate; and the liquid, after removal of the sulphide of lead, is evaporated over the water-bath, the water being renewed from time to time, as it evaporates, in order to drive off the acetic acid. The resulting extract dissolved in the smallest possible quantity of boiling alcohol yields, on evaporation, crystals of mannite, while ligustrin remains dissolved, and must be separated as completely as possible from admixed sugar by repeated treatment with strong alcohol.

In this manner a hygroscopic honey-yellow extract is obtained having a bitter taste, but still containing sugar, acetic acid, and acetates. This extract dissolves readily in water and in weak spirit, not in absolute alcohol or ether; it is not precipitated by alkalis or metallic salts, not even by basic acetate of lead until it is oxidised. Its aqueous solution, if not too concentrated, acquires, when mixed with oil of vitriol, a fine blue colour, like that of the corn-flower. When boiled with dilute sulphuric acid, it yields a resin insoluble in water, and likewise turning blue when its alcoholic solution is mixed with oil of vitriol.

If, according to Kromayer, the bark be exhausted with hot water, the decoction precipitated by basic acetate of lead, the lead removed from the filtrate by hydrosulphuric acid, and the liquid evaporated, a bitter syrup is obtained which gives up ligustropicrin to charcoal, and ligustrone to ether, while ligustrin remains in solution. — The syrup containing ligustrin has a sweet taste, and exhibits the blue colouring with oil of vitriol. When boiled with dilute sulphuric acid, it deposits brown tasteless lumps, which are neutral, dissolve with cherry-red colour in alcohol, and separate therefrom in red translucent granules; they give off 6·4 p. c. water at 100°, and in other respects resemble syringenin (p. 160).

Ligustrone.

KROMAYER.   *loc. cit.*

Crystallises from the syrupy solution in radiating needles, which melt to a yellow oil at a temperature somewhat above 100°, distil between 260° and 280°, emitting an odour of melilot, and solidify in the crystalline form on cooling. — Neutral.   Has a warming bitter taste. — Colours oil of vitriol yellowish. — Reduces ammoniacal silver-solution. — Easily soluble in water, alcohol, and ether.

COMPOUNDS CONTAINING 28 AT. CARBON.

Primary Nucleus $C^{28}H^{10}$.

Anthracene.

$C^{28}H^{10}$.

DUMAS & LAURENT.   *Ann. Chim. Phys.* 50, 187 ; *Ann. Pharm.* 5, 10 ; *Schw.* 66, 79 ; *N. Tr.* 26, 1, 206.
LAURENT.   *Ann. Chim. Phys.* 60, 220 ; 66, 149 ; further 72, 415 ; *Ann. Pharm.* 34, 287.
FRITZSCHE.   *Petersb. Acad. Bull.* 16, 150 ; *J. pr. Chem.* 73, 283 ; abstr. *Ann. Pharm.* 109, 249 ; *Chem. Centr.* 1858, 177.
TH. ANDERSON.   *Ann. Pharm.* 122, 294 ; *Edinb. Roy. Soc. Transact.* 22, 3, 681.

Paranaphthalin, Paranaphthalèse, Paranaphtalène.

Discovered in 1832 by Dumas & Laurent.   Reichenbach (*Schw.* 68, 239 ; *Pogg.* 28, 498) regarded anthracene as a mixture of naphthalin and paraffin, or confounded it with chrysene (xv. 1).   A hydrocarbon, described as new by Fritzsche, was recognised by Anderson as anthracene.

Formation.   Anthracene passes over in the dry distillation of coal (of bituminous shale, according to Laurent; of wood, according to Reichenbach), and is found in the tar.   It is contained only in the last heavy and semi-fluid portions of the coal-tar, at first together with naphthalin, finally with chrysene (Dumas & Laurent).   A commercial product of this kind, used as a lubricator for machinery, is yellow, soft, somewhat like palm-oil, and contains, besides anthracene, a small quantity of naphthalin, and a much less volatile empyreumatic oil. (Anderson.)

Preparation.   Crude commercial anthracene is distilled from an iron retort, and the colourless portions which pass over at the beginning, are pressed to remove the oil, and purified by repeated crystallisation from benzol, or by sublimation.   The coloured portions which pass

over at a later stage of the distillation, are obtained colourless by repeated rectification, then purified in the same manner (Anderson).

From the last liquid products of the distillation, anthracene is obtained in grains by cooling; from the following semi-fluid portions, only after they have been dissolved in the smallest possible quantity of oil of turpentine, and the solution cooled to $-10°$. The granules are washed with alcohol, and distilled two or three times (Dumas & Laurent).

Fritzsche immediately dissolves anthracene, obtained by pressure and recrystallisation, in boiling benzol, together with excess of picric acid, whereby crystals of the picrate are obtained on cooling. From this, the anthracene may be separated by ammonia, and purified by recrystallisation from alcohol.

Properties. Small colourless laminæ, which exhibit a silky lustre when immersed in alcohol, but become dull when dry. The laminæ which separate from solution in benzol, are less lustrous and somewhat granular (Anderson). Melts at 213° (at 180°, according to Dumas & Laurent; at about 210°, according to Fritzsche) to a colourless liquid, which solidifies to a foliated-crystalline mass on cooling. It sublimes slowly at the heat of the water-bath, more quickly in thin laminæ, at a stronger heat, and distils, without decomposition, at a still higher temperature (Anderson), above 300° according to Dumas & Laurent. Inodorous if free from empyreumatic oil. Tasteless. Sp. gr. 1·147 (Reichenbach). — Vapour-density = 6·74 at 450° (Dumas & Laurent).

				Dumas & Laurent.		Fritzsche.		Anderson. *mean.*
28 C	....	168	....	94·38	....	92·32	.... 94·16	94·16
10 H	....	10	....	5·62	....	6·05	.... 5·74	5·86
$C^{28}H^{10}$	....	178	....	100·00	....	98·37	.... 99·90	100·02

	Vol.	Vapour-density.
C-vapour	28	.... 11·648
....	10	.... 0·693
Anthracene-vapour	2	.... 12·341
	1	. ... 6·170

Dumas & Laurent gave the formula $C^{20}H^8$, afterwards $C^{30}H^{12}$. — Succisterin $C^{30}H^{10}$ is possibly the same substance.

Decompositions. 1. Anthracene dissolves in *oil of vitriol*, with green colour, and forms a conjugated acid (Dumas & Laurent, Anderson). — 2. In contact with *bromine*, either liquid or gaseous, it is slowly converted into hexbromanthracene (Anderson).

3. Anthracene exposed to a slow current of *chlorine-gas* for not too long a time, is converted into hydrochlorate of chloranthracene, a small quantity of hydrochloric acid gas being evolved at the same time. Exposed for a short time to a rapid current of chlorine, it becomes heated, and forms hydrochloric acid and chloranthracene. — When heated in chlorine gas, it absorbs a much larger quantity, gives off larger quantities of hydrochloric acid, and exhibits an increasing amount of chlorine, till after eight days, a semi-solid product is obtained, which, by solution in ether and evaporation, is resolved into

an oily and a crystallisable chlorine-compound (Anderson). — The crystals are soluble in alcohol, ether and benzol; contain 47·5 p. c. C., and 2·56 H., and are, perhaps, $C^{28}Cl^5H^9$ (calc. 47·39 p. c. C., 2·54 H.) or perhaps a mixture. — The oil treated with alcoholic potash, yields more than one crystallisable substance (Anderson).

4. Anthracene is but slightly attacked by cold *nitric acid;* but by boiling for several days with nitric acid of sp. gr. 1·2 it is converted into oxanthracene. Nitric of sp. gr. 1·4 likewise forms oxanthracene, but mixed with other products; if fuming nitric acid be added at the same time, binitroxanthracene is also produced. These compounds separate out on cooling, whilst a crystallisable acid remains in the mother-liquor. — This substance, Anderson's *anthracenic acid,* obtained by careful evaporation, is easily soluble in water, and forms crystallisable compounds with ammonia and potash, insoluble salts with baryta and oxide of lead (Anderson).

Laurent, by treating anthracene with nitric acid, obtained four nitro-compounds (and oxanthracene), the formulæ and independent existence of which are doubtful.

When 4 or 5 grammes of anthracene are boiled for a few seconds with nitric acid, red vapours are evolved, and a reddish-yellow layer is formed, containing small crystalline needles. The acid is removed, and the product is washed with boiling water and treated with ether, which leaves behind a portion (A). The residue left after evaporating the ether, may be separated by re-solution in ether, into an insoluble portion B., and a solution, which, when evaporated, leaves a soft residue C., which solidifies after the ether has been completely driven off.

A. Laurent's *Nitrite d'anthracénise.* — Purified by washing with cold, and solution in a very large quantity of boiling ether, whereupon it separates by cooling and spontaneous evaporation, in small acute yellow prisms. — Melts at a high temperature, and solidifies to a crystalline mass, which becomes covered with needles. Detonates when quickly heated in a test-tube. — Dissolves in oil of vitriol, and is precipitated by water. — Decomposed with difficulty by boiling alcoholic potash. — Sparingly soluble in alcohol, and in boiling ether. — Contains 71·4 p. c. C., 3·8 H., 5·9 N., and 18·9 O., whence, according to Laurent, it is $C^{30}H^9O^4$, NO^3, or $C^{30}H^8O^4$, NO^3.

B. Laurent's *Binitrite d'anthracénèse.* — Precipitated from solution in boiling ether, by cooling and spontaneous evaporation, as a yellow, scarcely crystalline powder. Inodorous, melts at a high temperature, and solidifies on cooling to a solid mass made up of long needles. When heated in a test-tube, it gives off vapours, which condense in yellowish flocks. When quickly heated, it deflagrates, with reddish light, and leaves a large quantity of charcoal. It dissolves in oil of vitriol, with brown colour, and in boiling alcoholic potash, with red-brown colour; from the latter solution, acids throw down a brown precipitate. — Insoluble in water, sparingly soluble in boiling alcohol, more soluble in ether, but less easily than A. — Contains 63·82 p. c. C., 3·44 H., 9·56 N., and 28·18 O., agreeing with the formula $C^{30}H^{10}O^2,2NO^3$.

C. *Trinitrite hydraté d'anthracénise.* — Orange-red resin, very fusible and very soluble in ether, detonating when suddenly heated, and yield-

ing by slow evaporation, acid vapours, a crystalline sublimate, and a residue of charcoal. — Contains 51·1 p. c. C., 3·6 H., and consists of $C^{30}H^9O^3,3NO^3$ (Laurent).

D. *Nitrite hydraté d'anthracénose.* — If the mixture obtained in the purification of the preceding products is boiled with nitric acid for several hours or till it is completely dissolved, the liquid on cooling deposits, in the course of 24 hours, needles having a faint yellowish colour, and water added to the mother-liquors throws down an additional quantity. These crystals are washed with water and alcohol. — The compound is fusible and solidifies in a mass of needle-shaped crystals; gives off a flocculent crystalline substance when kept for some time in a state of fusion, and leaves charcoal. When quickly heated it detonates, and emits light. Sparingly soluble in alcohol and ether. Contains 66·5 p. c. C., 3·6 H., 5·8 N., and 24·1 O., therefore perhaps $C^{30}H^8O^4,NO^3,HO$. (Laurent.)

Anthracene is insoluble in *water.* — It is not altered by *alkalis.* — It dissolves easily in boiling *alcohol,* more abundantly in *ether, benzol,* and *volatile oils* (Anderson); especially in *oil of turpentine* (Dumas & Laurent).

Compound with Picric Acid. —When anthracene is dissolved, together with excess of picric acid, in boiling benzol, the liquid on cooling deposits deep ruby-coloured crystals, about two lines long (Fritzsche). — Right-angled, probably quadratic prisms, with perpendicular end-faces (Kokscharoff). Melts at about 170°. Decomposed wholly or partially, by water, alcohol and ether, picric acid then dissolving. When decomposed by ammonia, it yields on the average 56·27 p.c. picric acid, and 44·00 p. c. anthracene (calc. 56·26 picric acid, and 43·74 p. c. $C^{28}H^{10}$) (Fritsche).

					Fritzsche.	Anderson.
40 C	240	.....	58·97	....	58·94	.... 58·71
3 N	42	....	10·32			
13 H	13	....	3·19	....	3·11	.... 3·54
14 O	112	....	27·52			
$C^{12}H^3X^3O^2,C^{28}H^{10}$	407	....	100 00			

Chlorine-nucleus $C^{28}ClH^9$.

Chloranthracene.

$C^{28}ClH^9$.

ANDERSON. *Ann. Pharm.* 122, 306,

Produced by the action of a rapid stream of chlorine on anthracene continued for a short time only, or by the action of alcoholic potash on hydrochlorate of chloranthracene.

Small hard, crystalline scales, soluble in *alcohol, ether,* and *benzol.*

		Scales.			Anderson.
28 C	....	168·0	....	79·06	.... 78·74
Cl	....	35·5	....	16·70	
9 H	....	9·0	.....	4·24	.... 4·46
$C^{28}ClH^9$	....	212·5	....	100·00	

Hydrochlorate of Chloranthracene.

$$C^{28}Cl^2H^{10} = C^{28}ClH^9,HCl.$$
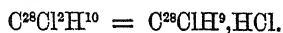
LAURENT.   *Ann. Chim. Phys.* 72, 424.
ANDERSON.   *Ann. Pharm.* 122, 306.

Chloranthracènèse (Laurent), *Bichloride of anthracene* (Anderson).

Compare page 166.   Cold chlorine gas is passed in a slow stream over anthracene, and the resulting mass is crystallised by solution in benzol and cooling.   Laurent introduces pulverised anthracene into a bottle filled with chlorine, dissolves out the anthracene which remains unaltered after 48 hours, with a small quantity of boiling ether, and crystallises the undissolved portion from a large quantity of boiling ether.

Radiate needles often very long (Anderson); yellowish, shining laminæ, fusible and volatile (Laurent).

				Laurent.		Anderson.
						mean.
28 C	168	....	67·47	.... 68·30	....	67·82
2 Cl	71	....	28·51			28·40
10 H	10	....	4·02	.... 3·80	....	4·03
$C^{28}ClH^9,HCl$	249	....	100·00			100·25

According to Laurent, $C^{30}Cl^2H^{10}$.

Easily soluble in *alcohol*, to which also it gives up a small quantity of hydrochloric acid. — *Alcoholic-potash* converts it into chloranthracene. — Slightly soluble in *ether*.

Derivatives and Conjugated Compounds of Anthracene.

Bromide of Bromanthracene.

$$C^{28}Br^4H^8 = C^{28}Br^2H^8,Br^2 ?$$

ANDERSON.   *Ann. Pharm.* 122, 304.

When an alcoholic solution of potash is poured upon the crystals of hexbromanthracene, they assume a sulphur-yellow colour, swell up strongly, and are resolved into bromide of potassium and this compound.   The transformation is completed by application of heat, and the product is collected, washed and dried, and crystallised from benzol.

Long yellow needles, having a fine silky lustre, which melt, with partial decomposition, at 238°.   They are nearly insoluble in cold benzol; boiling benzol is its best solvent, but even of this it requires more than 100 times its weight; it is still less soluble in alcohol and ether, either hot or cold.

				Anderson.		
				mean.		
28	C	168	....	33·87	....	34·02
4	Br	320	....	64·52		
8	H	8	....	1·61	....	1·57
$C^{28}Br^4H^8$		496	....	100·00		

Hexbromanthracene.

$$C^{28}H^{10}Br^6.$$
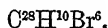
ANDERSON. *Ann. Pharm.* 122, 308.

A thin layer of pulverised anthracene is placed, together with bromine, under a bell-jar; the mass which forms after a few days is pulverised, and again exposed to the bromine-vapours; and this treatment is repeated as long as the bromine continues to be absorbed. The brown mass is dissolved in benzol, and the solution, on cooling, deposits crystals, which are recrystallised from ether or from benzol.

Small, white, hard, apparently rhombic crystals.

				Anderson.		
				mean.		
28	C	168	....	25·53	....	25·69
6	Br	480	....	72·95	....	72·33
10	H	10	....	1·52	....	1·63
$C^{28}Br^6O^{10}$		658	....	100·00	....	99·65

Anthracene turns brown at 176°, and melts at 182°, with evolution of bromine. When heated with *oil of vitriol*, it melts, and gives off bromine and hydrobromic acid. It is but slightly attacked by *nitric acid.* — With *alcoholic potash* it acquires a yellow colour, and forms bromide of potassium and bromide of bromanthracene $C^{28}H^8Br^4$.

Sparingly soluble in *alcohol, ether,* and *benzol.*

Oxanthracene.

$$C^{28}H^8O^4.$$

LAURENT. *Ann. Chim. Phys.* 66, 220; 72, 422.
ANDERSON. *Ann. Pharm.* 122, 301.

Paranaphtalèse. Anthracenuse.

Formation. 1. By boiling anthracene with nitric acid (Laurent, Anderson). — 2. Sublimes when *nitrite of anthracenose* (D. p. 167) is heated; perhaps also in the decomposition by heat of the other nitro-compounds of anthracene (Laurent).

Preparation. Anthracene is boiled for some days with nitric acid of sp. gr. 1·2, whereupon red vapours are given off, and a resin is formed, which solidifies in the granular state on cooling. This resin

is washed with water, and purified by recrystallisation from alcohol or benzol (Anderson).

Laurent boils anthracene with nitric acid, till it is completely converted into *nitrite of anthracenose*, subjects the product to dry distillation, and purifies the sublimate from adhering resin by washing with ether. Anthracene may also be boiled in a retort with nitric acid till all the acid is volatilised, oxanthracene then subliming towards the end of the process, while other products formed at the same time are decomposed (Anderson).

Properties. Light reddish-yellow crystals (colourless, according to Laurent), without taste or smell. From solution in alcohol the compound is deposited in long needles : from benzol in shorter and more compressed crystals. Fusible, volatile without decomposition ; sublimes in long beautiful needles. Neutral. Free from nitrogen (Laurent, Anderson).

| | | | | Laurent. | | | | Anderson. |
				earlier.		later.		mean.
28 C	168	....	80·77	....	80·4	....	78·17	....	80·53
8 H	8	...	3·85	....	3·6	...	3·47	....	3·97
4 O	32	....	15·38	...	16·0	...	18·06	....	15·50
$C^{28}H^8O^4$	208	....	100·00	....	100·0	....	100·00	....	100·00

Laurent gave the formulæ $C^{30}H^8O^4$ and $C^{30}H^7O^5$.

Oxanthracene *burns* on platinum-foil with a smoky flame and without residue (Laurent). — It is not altered by hot *hydrochloric acid*, by *potash-ley*, or *quick-lime* (Laurent), not even when sublimed over quick-lime (Anderson). — When oxanthracene is heated in a test-tube with concentrated *hydriodic acid*, white scales resembling stilbene condense in the upper part of the tube (? $C^{28}H^8O^4 + 8HI = C^{28}H^{12} + 8I + 4HO$) (Anderson).

Insoluble in *water*. Dissolves in cold *oil of vitriol*, forming an orange-coloured solution, and in hot oil of vitriol, forming a deep red solution, and is precipitated in its original state by water. — Dissolves in boiling nitric acid of sp. gr. 1·4, and crystallises on cooling (Anderson).

Sparingly soluble in *alcohol* (Anderson), nearly insoluble in boiling *ether*, and in hot *coal-tar oil* (Laurent). Somewhat more soluble in *benzol* than in alcohol (Anderson).

Binitroxanthracene.

$$C^{28}N^2H^6O^{12} = C^{28}X^2H^6O^4.$$
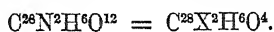
ANDERSON. *Ann. Pharm.* 122, 302.

When anthracene is boiled with nitric acid, and portions of the fuming acid are added from time to time, red fumes are continuously evolved, and the anthracene is converted into a resinous mixture of oxanthracene and binitroxanthracene. From this mixture the binitroxanthracene may be separated by heating with a small quantity of alcohol and cooling, as a red powder having very little of the crystalline character.

					Anderson.
28 C	...........: 168	. ....	56·37	....	58·66
2 N	 28	.. ....	9·40		
6 H	 6	.. ....	2·02	....	2·73
12 O	 96	....	32·21		

$C^{28}X^2H^6O^4$ .... 298 . ... 100·00

Primary Nucleus $C^{28}H^{14}$; *Oxygen-nucleus* $C^{28}H^{10}O^4$.

Chrysophanic Acid.

$C^{28}H^{10}O^4,O^4$; more correctly $C^{28}H^{10}O^6 = C^{20}H^8O^2,O^4$.

ROCHLEDER & HELDT (1843). *Ann. Pharm.* 48, 12.
SCHLOSSBERGER & DÖPPING. *Ann. Pharm.* 50, 213.
R. THOMPSON. *Phil. Mag J.* 25, 39; *N. Edinb. Phil. J.* 37, 187; *J. pr. Chem.* 33, 210; *Ann. Pharm.* 53, 252.
ROCHLEDER. *Wien. Akad. Ber.* 17, 169; *J pr. Chem.* 66, 246.
WARREN DE LA RUE & H. MÜLLER. *Chem. Soc. Qu. J.* 10, 300; *J. pr. Chem.* 73, 443.
v. THANN. *Wien. Akad. Ber.* 31, 26; *Ann. Pharm.* 107, 324; abstr. *J. pr. Chem.* 75, 247.
O. HESSE. *Ann. Pharm.* 117, 348.
ROCHLEDER & PILZ. *Wien. Akad. Ber.* 44, 493; *J. pr. Chem.* 84, 436; *Chem. Centr.* 1862, 6.

Rheic acid. Parietic acid. Parietin.—Discovered by Schrader (*Berl. Jahrb.* 1819) who named it *resinous yellow of wall lichen* (*harziges Wand-flechtengelb*); described by Herberger (*Repert.* 47, 202) as *Parmelia-yellow;* prepared pure and investigated by Rochleder & Heldt. Schlossberger & Döpping afterwards found chrysophanic acid in rhubarb-root.

The earlier attempts to separate the active constituent of rhubarb-root, led to the preparation of mixtures containing resins, extractive matters and chrysophanic acid. To these belong the *Rhabarberstoff* of Trommsdorff (*A. Tr.* 3, 1, 106); the *rhubarb-bitter* of Schrader (*Berl. Jahrb.* 1807, 23), and Pfaff (*Syst.* 3, 23, and 6, 308), the *rheumin* of Hornemann (*Berl. Jahrb.* 1822, 252), the *rhabarberin* of Buchner & Herberger (*Repert.* 38, 368). Or the experiments led to the preparation of resins. Comp. Henry (*Bull. Pharm.* 6, 101), Peretti (*J. Pharm.* 14, 536).—Ridofi (*Ann. génér.* 5, 511; *Schw.* 32, 490), Nani (*Bibl. univ.* 23, 232), and Carpenter (*Sill. Am. J.* 9, 91; *Kastn. Arch.* 8, 294; *Mag. Pharm.* 15, 144) endeavoured to prepare a base from rhubarb. They described impure substances, which, according to Caventou (*J. gén. de méd.* 111, 157) and Rahn-Escher (*Schweiz. ärzt. Verh.* 1828, 165) were partly of inorganic nature, and, according to Carpenter (*Sill. Am. J.* 14, 33), did not even contain the active constituent of rhubarb. — The *rhubarb-yellow* and *rhabarbic acid* of R. Brandes (*Ann. Pharm.* 9, 85; *N. Br. Arch.* 6, 15), the *rhabarberin* of Geiger (*Ann. Pharm.* 9, 91 and 304), the *rhubarb-yellow* of Jonas (*N. Br. Arch.* 9, 245), the *rhein* of Dulk (*N. Br. Arch.* 17, 26) and O. Henry (*J. Pharm.* 22, 398) may be regarded as chrysophanic acid containing more or less resin. — The

rhein obtained by Vaudin (*Ann. Chim. Phys.* 34, 199 ; *Repert.* 26, 108 ; *Mag. Pharm.* 15, 145) from rhubarb with help of nitric acid, which was also prepared by Geiger (*Ann. Pharm.* 9, 304) and Garot (*N. J. Pharm.* 17, 5 ; *J. Chim. méd.* 25, 681) probably also belong to chrysophanic acid.

Hornemann's crystalline *rhaponticin* from the root of *Rheum rhaponticum* consists, according to Weppen (*Handwörterb.* 6, 827) of chrysophanic acid. The same is true, as shown by v. Thann, of the *lapathin* obtained from the root of *Rumex Hydrolapathum* by Buchner & Herberger (*Repert.* 38, 360) which was prepared by Geiger (*Ann. Pharm.* 9, 310) and Riegel (*Jahrb. pr. Pharm.* 4, 72) in a state of greater purity as *rumicin*, its resemblance to rhabarberin having previously been recognised by Geiger.

Occurrence. In *Parmelia parietina* (Schrader, Rochleder & Heldt). In *Squamaria elegans* (Thomson). — In the roots of the various species of *Rheum*, which yield the rhubarb of commerce (Schlossberger & Dopping). In the root of *Rumex obtusifolius* and *R. patientia* (Geiger, v. Thann). *Rumex maritimus*, *R. palustris* and *R. hydrolapathum* also contain chrysophanic acid, most abundantly in the root, less in the leaves and flowerstalks (H. Grothe, *Chem. Centr.* 1862, 107). — German rhubarb-root contained 7·5 p. c. chrysophanic acid (Bley & Diesel, *N. Br. Arch.* 49, 121).

Preparation. 1. *Parmelia parietina* or pulverised rhubarb-root is exhausted with weak spirit containing potash ; the liquid strained off, the residue pressed ; carbonic acid passed through the liquid ; and the resulting precipitate dissolved in alcohol of 50 p. c., to which a small quantity of hydrate of potassium has been added ; the liquid is then filtered and precipitated with acetic acid. The precipitate separated by filtration is dissolved in boiling alcohol, and the solution is filtered hot and water added, whereby chrysophanic acid is separated in yellow flocks, which may be purified by recrystallisation from alcohol (Rochleder). — 2. *Parmelia parietina* is digested with a mixture of alcohol and ammonia (or better, caustic potash), and the filtered extract is neutralised with acetic acid. The yellow flocks which separate are washed by decantation with water, as long as the water continues to take up anything from them ; they are then dissolved in spirit containing potash, and the solution is precipitated with acetic acid. The precipitate, washed with water and dried at 100°, is boiled with a small quantity of absolute alcohol, and the filtered solution is left to cool slowly. The greater part of the chrysophanic acid then separates in golden-yellow crystals, which may be obtained quite pure by repeating the process (Rochleder).

3. The alcoholic extract of rhubarb is washed with water, as long as the water takes anything from it ; the insoluble residue is dried over the water-bath, and dissolved in the smallest possible quantity of alcohol of 80 p. c. ; and this solution is mixed with ether, which throws down a mixture of aporetin, phæoretin, and resin. The dry chrysophanic acid obtained from the filtrate by distilling off the ether and evaporating, is purified by redissolving it in the smallest possible quantity of alcohol, mixing the solution with ether, again evaporating the filtrate, and recrystallising the residue from ether. The crystals

thus obtained are washed with cold ether, which, after the resin has been removed, dissolves but little of the chrysophanic acid (Schlossberger & Döpping). — 4. Pulverised rhubarb-root macerated with water and dried again, is exhausted in a percolator with commercial benzol (or light coal-tar oil) and the greater part of the benzol is distilled off, the residue then solidifying on cooling to a crystalline pulp. This is pressed between bibulous paper, and purified by solution in hot benzol, from a sparingly soluble reddish-yellow body, which partly remains behind, partly separates from the slightly cooled liquid. The solution is left to crystallise, and the resulting crystals are purified by several recrystallisations, first from benzol, and finally from glacial acetic acid, amylic alcohol, or common alcohol. By this process, chrysophanic acid may be obtained from the residue of the preparation of alcoholic rhubarb-tincture (which yields 2·6 p. c. of it), and from the deposit which forms in this tincture (De la Rue & Muller). — 5. The coarsely pounded roots of *Rumex obtusifolius* are exhausted in a percolator with anhydrous ether; the greater part of the ether is distilled off; the brown mass which separates after cooling, is collected on a filter, washed with a small quantity of ether, and dissolved after drying in spirit of 90 p. c.; the dirty green granular mass which separates on cooling, is purified by repeated solution in alcohol and precipitation by water; and the purification is completed by repeated application of the treatment described at page 172, 2 (Riegel, v. Thann).

Older methods. The ethereal extract of rhubarb-root is freed by distillation from the greater part of the ether, and the crystals which separate from the remaining liquid are purified by repeated crystallisation from alcohol of 75 p. c. (Brandes). — Alcoholic tincture of rhubarb is suspended in a large quantity of cold water; the undissolved portion is dissolved in boiling water; the impure chrysophanic acid, which separates after cooling is freed from foreign matters by repeated solution in boiling water and deposition by cooling, then dissolved in anhydrous alcohol; the alcohol is distilled off; the residue dissolved in ether free from water and alcohol; and the greater part of the ether is distilled off at a gentle heat (Geiger). — The turbid aqueous solution of rhubarb-extract is mixed with excess of caustic ammonia; solution of alum is added as long as a red precipitate is thereby produced; this precipitate is decomposed by dilute sulphuric acid; and the separated chrysophanic acid is purified by recrystallisation from alcohol, and then from ether (Geiger) — The alcoholic extract of the root of *Rumex patientia* is suspended in a large quantity of cold water; the portion which remains undissolved is washed with cold water and covered while still moist, with ether; the ethereal solution is left to evaporate, and the residue is washed with alcohol and then with ether (Geiger). Riegel distils the greater part of the ether from the ethereal extract of the root of *Rumex obtusifolius*, and purifies the crystals, which separate on cooling, by repeated crystallisation from alcohol of 75 p. c.

Purification according to Rochleder & Pilz. The alcoholic solution is mixed with neutral acetate of lead, and filtered, the filtrate is freed from lead by sulphuric acid; and the crysophanic acid is precipitated by water and repeatedly crystallised from alcohol, whereupon the resin dissolves chiefly at first, the purest chrysophanic acid appearing to be the least soluble.

Properties. Delicate orange-yellow interlaced needles, having a golden lustre like iodide of lead (Rochleder & Heldt). From benzol it is obtained in orange-yellow six-sided plates belonging to the oblique prismatic system ; from ethylic alcohol, amylic alcohol, or glacial acetic acid, in moss-like crystalline groups. — Melts at 162°, and solidifies in the crystalline form on cooling (De la Rue & Müller). — When cautiously heated, it sublimes partly undecomposed. — Nearly tasteless. It exerts a purgative action, equal to that of the less pure rhein and rhabarberin, but weaker than that of rhubarb (Schroff).

Calculations :

according to Rochleder & Heldt.				*according to* Gerhardt.			
20 C	120		68·12	28 C	168		69·42
8 H	8		4·54	10 H	10		4·13
6 O	48		27·34	8 O	64		26·45
C^{20}H^{8}O^6	176		100·00	C^{28}H^{10}O^8	242		100·00

Analyses.

	Rochleder & Heldt. *mean.*	Schlossberger & Döpping.	De la Rue & Muller.
C	68·05	68·16	68·76
H	4·59	4·24	4·25
O	27·36	27·60	26·99
	100·00	100·00	100·00

	v. Thann. *mean.*	Pilz. *a.*	*b.*	*c.*
C	69·62	69·08	68·48	68 00
H	4·47	4·61	4 65	4·51
O	25·91	26·31	26 87	27·49
	100·00	100·00	100·00	100 00

Dried at 100°. From *Parmelia* (Rochleder & Heldt) ; from rhubarb (Schlossberger & Döpping ; De la Rue & Müller) ; from the root of *Rumex obtusifolius* (v. Thann). — Gerhardt's formula was shown to be incorrect by Rochleder & Pilz, from whose experiments it appears that only impure chrysophanic acid exhibits a proportion of carbon higher than that required by the formula C^{20}H^{8}O^6 ; in Pilz's analyses *b* is purer than *a*, and *c* is the purest of all. — The names *parietin* and *oxide of parietin* were given by Thomson to two substances which he found to contain 65·8 and 63·6 p. c. carbon respectively, and regarded as C^{40}H^{16}O^{14} and C^{40}H^{16}O^{16}, but they were really nothing but impure chrysophanic acid. — The rhabarbic acid analysed by Brandes & Leber (*N. Br. Arch.* 17, 42) contained 54·3 p. c. carbon and 4·6 hydrogen, and its baryta-salt 45·78 p. c. carbon, 3·98 hydrogen, and 16·56 baryta ; according to Hesse it is perhaps C^{70}H^{40}O^{40} and isomeric with ruberythric acid (p. 42) ; but rhabarbic acid resembles chrysophanic acid, and the correctness of the analyses on which Hesse's opinion was formed is doubtful (Kr.).

Decompositions. 1. When chrysophanic acid is strongly *heated*, part of it decomposes and another portion sublimes undecomposed. — 2. *Bromine* and *chlorine* appear to act but slightly on it, and do not alter the yellow colour ; but a mixture of *chlorate of potash and hydrochloric acid*, as well as *nitro-muriatic acid*, converts chrysophanic acid at the boiling heat into a liquid substance, which no longer crystallises on cooling, but is still coloured red by alkalis (De la Rue & Müller). — 3. Dilute *nitric acid* does not act on chrysophanic acid even at the boiling heat ; but strong nitric acid converts it into a red substance,

which forms a splendid violet-red solution with aqueous ammonia, is not altered by acetic acid, but when boiled with potash gives off ammonia, and deposits a violet substance, insoluble in water (Rochleder & Heldt). — 4. It is not altered by boiling or evaporation with potash-ley, but decomposes when fused for some time with *lumps of potash*, emitting an odour of caprylic alcohol (De la Rue & Müller); with evolution of hydrogen and formation of acids smelling like valerianic or caproic acid (Hesse). — 5. Chrysophanic acid dissolved in *oil of vitriol* is decomposed by addition of *peroxide of manganese* (De la Rue & Müller). —6. With *chloride of acetyl* it forms acetyl-chrysophanic acid:

$$2C^{20}H^8O^6 + 4C^4H^3O^2Cl = C^{56}H^{22}O^{18} + 4HCl + 2HO.$$
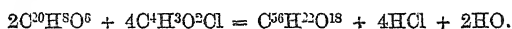
(Rochleder & Pilz). — 7. When a solution of chrysophanic acid in excess of potash-ley, from which, after standing for some time, part of the potash-salt has been deposited in violet-red flocks, is digested for some minutes in a closed flask with *grape-sugar*, the liquid, which has at first a violet-red colour, changes to brown-yellow and dissolves the flocks. If exposed to the air in a shallow vessel, it again deposits flocks, and acquires a red colour (De la Rue & Müller).

Combinations. Chrysophanic acid is nearly insoluble in cold *water*, somewhat more soluble in boiling water, to which it imparts a deep red colour (Schlossberger & Döpping). — It dissolves in *oil of vitriol* with splendid red colour, and is precipitated by water, unaltered and in yellow flocks (Schlossberger & Döpping).

It dissolves easily and with fine red colour in aqueous *ammonia* and the *fixed alkalis*, the ammoniacal solution gives off all its ammonia on prolonged boiling, and leaving the acid in its original state (Rochleder & Heldt).

Chrysophanate of Potash. — The solution of chrysophanic acid in excess of moderately dilute potash-ley, deposits, on standing or concentration, violet-red flocks of the potash-salt, which dissolve in water and in alcohol (Rochleder & Heldt, De la Rue & Muller).

Chrysophanate of Baryta. — When chrysophanic acid is boiled with baryta-water, red flocks are obtained, which turn yellow on exposure to the air, and are converted into a mixture of carbonate of baryta and chrysophanic acid (Rochleder & Heldt).

From *solution of alum*, ammoniacal chrysophanic acid throws down a precipitate of a fine rose-red colour (v. Thann).

Chrysophanate of Lead. — An ammoniacal solution of chrysophanic acid forms a lilac precipitate with neutral acetate of lead (v. Thann). From basic acetate of lead it throws down a dense white or yellowish precipitate, which changes to a carmine-coloured jelly on addition of water, and becomes cinnabar-red when dry. — If exposed to the air in the moist state, it acquires a yellow colour from partial decomposition; hence, the quantity of lead-oxide contained in it has been found to vary from 56·93 to 59·32 p. c. (Rochleder).

Chrysophanic acid dissolves at 30° in 1125 pts. of *alcohol* of 86 p. c., and in 224 pts. of boiling alcohol. It dissolves in *ether, glacial acetic acid, amylic alcohol,* and with peculiar facility in *benzol* and *coal-*

tar naphtha (De la Rue & Müller). — It dyes silk, woollen and linen stuff, prepared with tin mordants, and cotton mordanted with alum (Grothe, *Chem. Centr.* 1862, 107).

Appendix to Chrysophanic Acid.

1. *Emodin.* — Obtained in the preparation of chrysophanic acid from rhubarb (p. 173). The residue, which is but sparingly soluble in cold benzol, is completely dissolved in hot benzol; the solution is left to cool slowly; and the substance which separates is purified by recrystallisation from hot glacial acetic acid, and from boiling alcohol. — Shining, deep orange-coloured, brittle prisms, belonging to the oblique prismatic (monoclinic) system, often two inches long. Does not melt below 250°, but a small portion of it volatilises in yellow vapours, condensing to an oil which solidifies in the crystalline state. It contains, on ;the average, 66·63 p. c. carbon, 4·10 hydrogen, and 29·27 oxygen, answering to the formula $C^{40}H^{15}O^{13}$ (calc. 66·85 p. c. C., and 4·18 H.) Like chrysophanic acid, it dissolves in aqueous *ammonia*, forming a violet-red liquid, which, when evaporated, leaves a residue free from ammonia. With the aqueous solutions of the *fixed alkalis*, it behaves like chrysophanic acid, but dissolves more readily than that acid in *alcohol, glacial acetic acid*, and *amylic alcohol*, less easily than chrysophanic acid in *benzol* (Warren De la Rue & Müller, *Chem. Soc. Qu. J.* 10, 304; *J. pr. Chem.* 73, 443).

2. *Aporetin.* — When the mixture of aporetin phæoretin and resin precipitated by ether in the preparation of chrysophanic acid by method 3, is treated with alcohol, aporetin remains behind, and may be purified by solution in potash, precipitation with dilute sulphuric acid, and washing with water (Schlossberger & Döpping.) — The deposit which forms in alcoholic rhubarb-tincture after long standing is washed with alcohol, dissolved in potash-ley, precipitated by hydrochloric acid, and washed with water and alcohol successively (De la Rue & Müller). — Black, shining, very friable resin, containing 58·89 p.c. carbon, 4·35 hydrogen, and 36·76 oxygen (Schlossberger & Döpping).

When heated on platinum-foil it *burns away* without melting. — Boiling *nitric acid* converts it into oxalic acid and a yellow nitro-compound, probably chrysammic acid (xiv. 1) (De la Rue & Müller).

Aporetin is insoluble in *water*, but dissolves with brown colour in aqueous *ammonia* and *potash*. — It is nearly insoluble in *alcohol, ether, chloroform*, and *benzo l*.

3. *Erythroretin.* Does not occur in the root of German rhubarb (Bley & Diesel). — Remains dissolved in the ethereal mother-liquor, from which chrysophanic acid has crystallised (preparation 3, p. 172), and is obtained by evaporating the mother-liquor, as a nearly tasteless, rhubarb-yellow powder. — It contains, on the average, 63·01 p. c. carbon, 5·59 hydrogen, and 31·40 oxygen, corresponding to the formula $C^{38}H^{18}O^{14}$ (calc. 63·96 p. c. C., 4·98 H., and 31·06 O). — It softens in boiling water, melts when *heated*, gives off yellow fumes, and leaves difficultly combustible charcoal. — It is very little soluble in *water*, but imparts to it a faint yellow colour; dissolves in *oil of vitriol* with brown colour, and is precipitated therefrom by water. — Dissolves in aqueous

alkalis and in *ammonia*, with fine purple-red colour, and is precipitated by acids in yellow coherent flocks.

From solution of *neutral acetate of lead*, ammoniacal erythroretin throws down a violet-red precipitate, which alters quickly in air containing carbonic acid. Contains on the average 16·8 p.c. carbon, 1·36 hydrogen, 12·54 oxygen, and 69·27 oxide of lead, but is obtained of different composition by different modes of preparation.

Erythroretin dissolves easily in *alcohol*, less in *ether*, and in *acetic acid* (Schlossberger & Döpping).

4. *Phæoretin.* From the mixture of aporetin and phæoretin precipitated by ether in the preparation of chrysophanic acid by method 3 (p. 172), the phæoretin may be dissolved up by alcohol, and reprecipitated by ether. — Yellow-brown powder, having a faint odour of rhubarb when heated. — It contains, on the average, 59·80 p.c. carbon, 5·15 hydrogen, and 35·05 oxygen, corresponding with the formula $C^{32}H^{10}O^{14}$ (calc. 60·27 C., 4·95 H., and 34·46 O.) — *Heated* on platinum foil, it melts and gives off yellow vapours. — Colours *water* faintly yellow, and dissolves in it with difficulty. — Dissolves in *oil of vitriol*, and is precipitated in yellow flocks by water. — Dissolves easily with dark red-brown colour in aqueous *alkalis*, and is precipitated therefrom by acids. — From its ammoniacal solution *neutral acetate of lead* throws down a violet-red precipitate, which easily alters when washed with water and alcohol, and contains on the average 20·39 p. c. C., 1·60 H., 13·48 O., and 64·53 PbO. — Phæoretin dissolves readily in *alcohol*, and with yellow colour in *acetic acid* (Schlossberger & Döpping).

Conjugated Compound of Chrysophanic Acid.

Acetyl-chrysophanic Acid.

$$C^{56}H^{22}O^{18} = 2C^{20}H^7O^5,4C^4H^2O^2$$
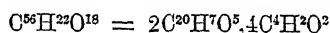
Rochleder & Pilz. *Wien. Akad. Ber.* 44, 493; *J. pr. Chem.* 84, 439; *Chem. Centr.* 1862, 6.

Formation and Preparation. When chrysophanic acid is gently heated on the water-bath with chloride of acetyl, the condensed vapours being allowed to flow back again, it dissolves to a brown yellow liquid with copious evolution of hydrochloric acid gas. From this liquid, the excess of chloride of acetyl is expelled by a stream of dry carbonic acid gas at 40°; the residual mass is completely covered with small quantities of ether, which takes up the resin; and the light yellow residue is dissolved in a large quantity of ether. The ethereal solution, filtered and evaporated, yields crystals of acetyl-chrysophanic acid, while a brown resin remains in the mother-liquor.

Small crystals, of a lighter yellow colour than chrysophanic acid.

56 C	....	336	.... . 66·93	....	66·81
22 H	....	22	...... 4·38	......	4·32
18 O	....	144	...... 28·69	....	28·87
$C^{56}H^{22}O^{18}$	....	502	.... 100·00	....	100·00

Acetyl-chrysophanic acid dissolves in *alcohol*, even when mixed with a large quantity of water; the solution, after standing for some time, is found to contain acetic and chrysophanic acids.

Gentianic Acid.

$$C^{28}H^{10}O^{10} = C^{28}H^{10}O^{4},O^{6}.$$
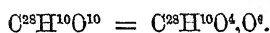
HENRY & CAVENTOU. *J. Pharm.* 7, 173 ; *N. Tr.* 6, 2, 79.
H. TROMMSDORFF. *Ann. Pharm.* 21, 134.
LECONTE. *J. Pharm.* 23, 465 ; *Ann. Pharm.* 25, 200.
BAUMERT. *Ann. Pharm.* 62, 106 ; abstr. *Pharm. Centr.* 1847, 549 ; *N. J. Pharm.* 13, 51.

Gentianin. Gentisic acid. Gentisin. — To be distinguished from gentian-bitter, the bitter principle of gentian root. — Discovered by Henry and Caventou; prepared pure by Trommsdorff; investigated chiefly by Baumert. — Occurs in the root of *Gentiana lutea* (*Handbuch*, viii. *Phytochem.* 58).

Preparation. 1. The powdered root is treated for several days with cold water, to remove the greater part of the gentian-bitter; the residue is pressed, washed, and exhausted with strong alcohol; the tincture thus obtained is evaporated to a syrup; water is added; and the substances soluble in water are separated, by treatment with several fresh portions of water, from the sediment, which contains gentianic acid, fat, resin, and gentian-bitter. This is freed from fat by ether, and purified by repeated crystallisation from strong alcohol (Leconte, Baumert). — 2. The powdered root is exhausted with ether, the ether distilled from the extract, and the residue treated with alcohol of 80 p. c. The tincture, separated from resin, and subjected to distillation in a water-bath, leaves a crystalline residue, which is washed repeatedly with small quantities of ether, and purified by washing with a little cold alcohol, pressing, and recrystallising from boiling alcohol (H. Trommsdorff). Yield $\frac{1}{2000}$ to $\frac{1}{1000}$ of the dried root.

Properties. Light, long, pale-yellow, silky needles. Permanent in the air. Unchangeable at 250° (Leconte); loses its lustre and turns brown at 200° (Baumert), at 300° (Leconte). Sublimes when cautiously heated (Trommsdorff), at 300–340° (Baumert), in yellow vapours, which condense in the form of fine yellow needles. According to Leconte and Baumert, the greater part is thereby carbonised; according to Trommsdorff, no residue remains. — Tasteless, neutral. — Without action on the organism in doses of several grammes (Leconte).

	Crystals.		Baumert. *mean.*
28 C.	168	65·11	65·06
10 H	10	3·87	4·16
10 O	80	31·02	30·78
$C^{28}H^{10}O^{10}$	258	100·00	100·00

Baumert's formula is half the above.

Decompositions. 1. By *heat* (p. 178). — 2. *Chlorine*, passed into an al-coholic solution of gentianic acid, separates pale yellow flakes containing chlorine. — 3. *Nitric acid* of sp. gr. 1·43 converts it into nitro-gentianic acid. From a solution in weaker nitric acid, gentianic acid is precipitated by water unchanged; it is not altered by very dilute nitric acid. On addition of gentianic acid to fuming nitric acid, a violent reaction occurs, increasing to ignition if the mixture be heated, in which case, part of the acid is carbonised. From the carefully prepared solution, water precipitates a yellow powder (see *Ternitro-gentianic acid*). Gen-tianic acid evaporated with nitric acid leaves a slight residue, free from oxalic acid. — 4. Melted with *caustic potash*, it is coloured, first brown, then lighter, without development of gas. On neutralising the liquid with dilute sulphuric acid, and evaporating, a black mass re-mains, from which alcohol takes up yellow needles of a potash-salt differing from oxalate of potash. — 5. On distillation with *bichromate of potash* and sulphuric acid, carbonic and formic acids are produced. — 6. Gentianic acid reduces *silver-salts* (Baumert).

Combinations. — With *Water.* — Gentianic acid dissolves in 5,000 parts cold, and in 3,850 parts boiling water (Leconte), in 3,030 parts water at 16° (Baumert).

It is not altered by aqueous *sulphurous, hydrochloric,* or *acetic* acid, and not more freely dissolved than by water (Baumert, Leconte). It remains unchanged after boiling for days with *dilute sulphuric acid* (Baumert).

Triturated with *anhydrous sulphuric acid,* if no heating takes place, it forms an olive-green liquid; *oil of vitriol* poured upon it produces a yellow solution. It is separated from these combinations by carbonate of baryta or by water, in its original state (Baumert).

With *Bases.* — Gentianic acid dissolves readily in aqueous alkalis, with fine golden-yellow colour; it expels carbonic acid from alkaline carbonates, and forms crystallisable compounds (Trommsdorff). It combines with bases in various proportions, without elimination of water. This behaviour requires further examination (Kr.). The moist salts of gentianic acid are partially decomposed by the carbonic acid of the air (Baumert). See also *Gentianate of soda.*

Gentianate of Potash. — a. *Mono-acid.* — When caustic potash and gentianic acid are boiled with alcohol of 90 p. c. until all the acid is dissolved, and the liquid is filtered from the undissolved potash, golden-yellow needles of b separate on cooling, and from the mother-liquor crystals of a are formed. These last lose 12·25 p. c. water at 100° (5 at. = 12 86 p. c. HO) (Baumert).

		at 100°.		Baumert.
28 C	168	....	55·05	.... 54·74
10 H	10	....	3·27	.... 3·51
10 O	80	....	26·22	.... 26·48
KO	47·2	....	15·46	.... 15·27
C²⁸H¹⁰O¹⁰,KO	305·2	....	100·00	.... 100·00

b. *Five-fourths?* — *Preparation,* see above. — Golden-yellow, silky needles, purified by washing with alcohol. — They give off 16·27 p. c. water at 100° (32 at = 16·30 p.c. HO.) (Baumert).

		at 100°.			Baumert.	
5	$C^{28}H^{10}O^{10}$	1290·0	....	87·23	
4	$\overline{K}O$	188·8	....	12·77	....	13·11
5	$C^{28}H^{10}O^{10},4\overline{K}O$	1478·8	....	100·00	

c. *Bi-acid.* — An alcoholic solution of gentianic acid is mixed with an aqueous solution of carbonate of potash in such proportion that no acid is separated; the mixture is evaporated; and the residue is exhausted with alcohol of 90 p. c., from which, after long standing, golden-yellow needles crystallise in radiated groups. They lose 4·67 p. c. water at 100° (3 at. = 4·5 p.c. HO.) (Baumert).

		at 100°.			Baumert.	
2	$C^{28}H^{10}O^{10}$	516·0	....	91·62	
	$\overline{K}O$	47·2	..	8·38	...	8·4
2	$C^{28}H^{10}O^{10},\overline{K}O$	563·2	...	100·00	

Gentianate of Soda. — The soda-salts of gentianic acid contain 1, 1½, ⁷⁄₄, and 3 at. acid to 1 at. soda. — They crystallise readily in golden-yellow needles having an alkaline reaction; those containing water of crystallisation deliquesce in the air. They are easily soluble in water and in alcohol, but are resolved by much water, or by repeated crystallisation from alcohol, into gentianic acid and soda. They are completely decomposed by carbonic acid.

a. *Mono-acid.* — The alcoholic solution of b is evaporated to dryness with carbonate of soda, and the residue exhausted with absolute alcohol. The crystals, purified by recrystallisation, are golden-yellow, and deliquesce in the air; they lose 20·14 p. c. water at 100° (8 at. = 19·93 p. c. HO), and turn brown. — Obtained also by dissolving gentianic acid in a solution of caustic soda, evaporating, and exhausting the residue with absolute alcohol (Baumert).   See also c.

		Dried.			Baumert.	
28	C	168	....	58·08	....	58·04
10	H	10	....	3·45	....	3·72
10	O	80	....	27·66	....	27·30
	NaO	31	....	10·81	....	10·94
	$C^{28}H^{10}O^{10},NaO$	289	....	100·00	....	100·00

b. *Sesqui-acid.* — Gentianic acid is boiled with alcohol and carbonate of soda, so long as anything is dissolved, and the needles which form on cooling are recrystallised from absolute alcohol. Contains no water of crystallisation (Baumert).

		Crystals.			Baumert.	
84	C	504	....	60·25	....	59·60
30	H	30	....	3·67	....	3·88
30	O	240	....	28·61	....	29·25
2	NaO	62	....	7·47	....	7·27
	$3C^{28}H^{10}O^{10},2NaO$	836	....	100·00	....	100·00

c. *Seven-fourths?* — When a solution of gentianic acid in caustic potash is evaporated almost to dryness, and the crystalline residue is dissolved in alcohol of 30°, long golden-yellow needles are obtained on cooling, which, at 100°, assume a reddish colour, and lose 23 p. c. of

their weight. They dissolve in 15·7 parts of cold, and in 10·7 parts of boiling alcohol of 30°; the solution deposits gentianic acid on cooling. They are decomposed also by water and by carbonic acid; the gentianic acid precipitated by the latter is white, but turns yellow when dried (Leconte).

According to Baumert.				Leconte.
7 $C^{28}H^{10}O^{10}$ 1806	....	93·58	....	
4 NaO 124	....	6·42	...	6·81
7 $C^{28}H^{10}O^{10}$,4NaO ... 1930	....	100·00		

d. *Ter-acid.* — A mixture of alcoholic gentianic acid with as much aqueous solution of carbonate of soda as can be added without throwing down the acid, is evaporated to dryness and exhausted with alcohol. — Crystals, giving off 10·12 p.c. water at 100° (10 at. = 10·05 p. c. HO.) (Baumert).

	at 100°.		Baumert.
3 $C^{28}H^{10}O^{10}$ 774	....	96·15	
NaO 31	....	3·85	.... 4·08
3$C^{28}H^{10}O^{10}$,NaO 805	....	100·00	

Gentianate of Baryta. — *Basic.* — An aqueous solution of chloride of barium or acetate of baryta precipitates nothing, or only the acid, from alcoholic gentianic acid. A solution of the acid in alcohol is precipitated with baryta-water, and the orange-coloured flakes are washed and dried in a vacuum over sulphuric acid and quick-lime. The salt absorbs carbonic acid rapidly from the air (Baumert).

Flakes.			Baumert.
$C^{28}H^{10}O^{10}$ 258	....	62·76	
2BaO 153	....	37·24	.... 37·80
$C^{28}H^{10}O^{10}$,2BaO 411	...	100·00	

Gerhardt (*Traité,* 3, 784) and Weltzien (*Verbind.* 591) suppose this compound to contain 2 at. water.

Gentianate of Lead. — *Basic.*—Ammoniacal neutral acetate and basic acetate of lead precipitate alcoholic gentianic acid in orange-coloured flakes. — If to an alcoholic solution of the acid, ammonia, and then neutral acetate of lead, be added, so that a part of the acid remains in solution, the salt *a* is obtained. Sometimes salts containing a smaller proportion of oxide of lead are precipitated. When a part only of the acid is thrown down from the alcoholic solution with basic acetate of lead, the precipitate has the composition *b* (Baumert).

				Baumert.	
				a.	*b.*
28 C........................ 168	....	23·86	....	23·60	.... 25·30
10 H 10	....	1·42	....	1·37	.... 1·46
10 O 80	....	11·36	....	11·58	... 12·00
4 PbO 448	...	63·36	..	63·45	... 61·24
$C^{28}H^{10}O^{10}$,4PbO 706	....	100·00	....	100·00	... 100·00

Baumert gives for *b* the formula 3$C^{28}H^{10}O^{10}$,11PbO.

Alcoholic gentianic acid precipitates *ferric salts* red-brown, *cupric salts* green.

Gentianic acid dissolves in 500 parts cold *alcohol* of 30°, and in 90 parts boiling alcohol of the same strength, crystallising on cooling; in 455 parts cold, and 62·5 parts boiling absolute alcohol (Leconte). —Soluble in 2,000 parts cold *ether* (Leconte).

Oxynitro-nucleus $C^{26}X^2H^8O^4$.

Binitrogentianic Acid.

$$C^{28}N^2H^8O^{18} = C^{28}X^2H^8O^4,O^6.$$
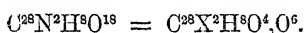
BAUMERT.   *Ann. Pharm.* 62, 122.

Nitrogentianin.

See page 178. Gentianic acid is added to nitric acid of sp. gr. 1·43 (free from nitrous acid), and the fine green solution thereby formed is precipitated by careful addition of water, with constant stirring.

Green powder, which, after drying in a vacuum, loses 3·97 p. c. water at 100° (2 at. = 4·92 p. c. HO).

		Dried in vacuo.			Baumert. mean.
28 C	....	168	.. 45·90	....	45·66
2 N	....	28	.... 7·65	....	7·76
10 H	... .	10	. 2·73	....	2·54
20 O	....	160	... 43·72	...	44·04
$C^{28}X^2H^8O^{10}$,2aq	....	366	.... 100·00	....	100·00

When binitrogentianic acid is boiled with solution of *caustic potash*, sulphuric acid precipitates from the solution reddish-yellow flakes, insoluble in alcohol.

In contact with *ammonia* or *alkalis*, it is immediately coloured cherry-red, and then becomes easily soluble in water, forming a deep red solution. On passing gaseous ammonia over it, 18·8 p. c. is taken up.

Oxynitro-nucleus $C^{28}X^3H^7O^4$.

Ternitrogentianic Acid:

$$? \; C^{28}N^3H^7O^{22} = C^{28}X^3H^7O^4,O^6.$$
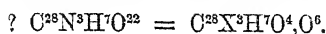
BAUMERT.   *Ann. Pharm.* 62, 125.

See page 178. When gentianic acid is added in small quantities at a time to fuming nitric acid (the violence of the reaction being allowed to subside before every fresh addition), a red solution is formed, from which water precipitates a pale-yellow powder, consisting of microscopic prisms, which may be freed from admixed amorphous portions

by washing with hot water (Baumert). This seems to be ternitrogentianic acid (Kr.).

		at 100°.				Baumert.		
28	C	168	....	42·74	....	42·73	....	41·46
3	N	42	....	10·69				
7	H	7	....	1·78	....	2·36	....	1·83
22	O	176	....	44·79				

$C^{28}X^3H^7O^{10}$ .... 393 .... 100·00

Baumert gives, as probable formulæ, $C^{14}N^2H^4O^{10}$ and $C^{14}N^2H^3O^{11}$.

Primary Nucleus $C^{28}H^{16}$; *Oxygen-nucleus* $C^{28}H^{14}O^2$.

Terebenzic Acid.

? $C^{28}H^{14}O^8 = C^{28}H^{14}O^2,O^6$.
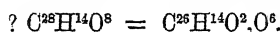
CAILLIOT. *N. Ann. Chim. Phys.* 21, 31; *J. pr. Chem.* 42, 233; *Pharm. Centr.* 1847, 201.

Obtained by distilling oil of turpentine with a large excess of nitric acid, as described at page 425, vol. xi, and exhausting the mixture of oxalic, terebic, terephtalic, and terebenzic acids, with boiling water; the terebenzic acid crystallises on cooling (*See also* xiii, 13).

Shining, white needles. Never crystallises in laminæ like benzoic acid. Sublimes in open vessels below 100°, melts at 169°, and boils at a much higher temperature.

					Cailliot.
					mean.
28	C	168	68·29		67·65
14	H	14	5·68		5·58
8	O	64	26·03		26·77

$C^{28}H^{14}O^8$ .... 246 .... 100·00 .... 100·00

The above is Weltzien's formula (*Verbind.* Braunschw. p. 587), Cailliot's is one-half of it.

Dissolves in boiling *water*, and distils over easily with water-vapour.

The *salts* of terebenzic acid resemble the benzoates. — The *silver-salt* contains 49·5 p. c. oxide of silver ($C^{28}H^{12}Ag^2O^8 = 50·4$ p. c. AgO). — Terebenzate of ethyl smells like *anise*, and boils at 130°.

Terebenzic acid dissolves freely in *alcohol* and *ether*.

Ellagic Acid.

$C^{28}H^6O^{16} = C^{28}H^6O^{10},O^6$.

BRACONNOT. *Ann. Chim. Phys.* 9, 187; *N. Tr.* 3, 2, 400.
PELOUZE. *Ann. Chim. Phys.* 54, 356; *Ann. Pharm.* 10, 163.
GUIBOURT. *Rev. scient.* 13, 38; abstr. *Ann. Pharm.* 48, 360. — *Rev. scient.* 14, 17. — *N. J. Pharm.* 10, 87.

MERKLEIN & WÖHLER. *Ann. Pharm.* 55, 129; abstr. *Compt. rend.* 21, 255.

FR. GÖBEL. *Ann. Pharm.* 79, 83.

AD. GÖBEL. *Ann. Pharm.* 83, 280.

Bezoardic acid, which name however is given also to lithofellic acid. *Ellagallic acid.* The statements of Fr. Göbel respecting urous acid (*harnige Säure*) refer to ellagic acid—First obtained by Chevreul, and recognised as an independent body by Braconnot.

Sources and Formation. Occurs ready formed in nutgalls (Guibourt), and is produced from the tannic acid contained in them (xv, 462) on their undergoing alcoholic fermentation (Braconnot); by decomposition with acids according to xv, 459, 460 (Rochleder & Schwartz), perhaps also with bisulphite of ammonia (xv. 461) (Knop). On exposing moist impure tannic acid to the air, Erdmann obtained ellagic acid without a trace of gallic acid (Liebig, *Ann. Pharm.* 26, 165). A decoction of nutgalls which had been precipitated with chloride of calcium, filtered, and set aside for several months in an open flask, threw down, first a dark powder, and afterwards, in intense cold, shining scales of a substance exhibiting the characters of a double lime-salt of hydrochloric and ellagic acids (Hünefeldt, *J. pr. Chem.* 7, 231). Not obtained by heating gallic acid with oil of vitriol, as is erroneously stated by Robiquet (xiv, 402, 412).

Oriental bezoars of a particular kind (infusible, and only slightly soluble in alcohol) contain ellagic acid (Merklein & Wöhler). Concerning these bezoars, see Guibourt (*Rev. scient.* 14, 17), Fr. Göbel (*loc. cit.*), and Ludwig (*N. Br. Archiv.* 85, 142). — Ellagic or a similar acid is found in castoreum (Wöhler, *Ann. Pharm.* 67, 361). Ellagic acid, together with an unknown product, may be recovered from glaucomelanate of potash (Merklein & Wöhler, xv, 25). Tormentil root contains ellagic acid (Grischow, *Kastn. Archiv.* 1, 481).

Preparation. From Nutgalls. Moistened powder of nutgalls is allowed to undergo alcoholic fermentation at a moderate temperature, whereby the tannic acid is converted into gallic and ellagic acids and decomposition-products of sugar. The fermented mass is then pressed between folds of linen, the residue boiled with water, and again subjected to pressure in a linen cloth. The strained liquid, which is rendered milky by the ellagic acid contained in it, is filtered while still hot; the yellowish-white powder remaining behind (consisting of ellagic acid, with colouring matter and gallate and sulphate of lime) is digested with dilute caustic potash; and the solution is filtered and left to evaporate in the air, when greenish-white scales of a potash-salt are deposited. These are washed with water and decomposed with hydrochloric acid (Braconnot). It would undoubtedly be better to precipitate the alkaline solution with carbonic acid, according to Merklein and Wöhler's method (Kr.). From the mixture of gallic and ellagic acids thus obtained, the former cannot be separated by crystallisation, nor can the latter (which remains suspended) be removed by filtration; the yellowish-white powder is therefore treated with hot alcohol, whereby the ellagic acid is left behind. It is freed from traces of gallic acid by boiling with water; dissolved in cold dilute caustic potash; and at once precipitated with an acid (Ph. Büchner, *Ann. Pharm.* 53, 185).

Ellagic acid is obtained in the purification of tannic acid according to

xv, 455 (Rochleder & Schwartz). When 100 gr. of powdered nutgalls are placed in a percolator and exhausted four times with a mixture of 300 parts ether, 15 parts alcohol of 90 p. c., and 5 parts water, and then twice with pure ether, three layers of liquid are formed, in the lowermost syrupy one of which small crystals of ellagic acid are deposited, together with luteogallic acid. When galls are extracted, first with ether and afterwards with alcohol, and the alcoholic extract is shaken with 1 part ether and 2 parts water, ellagic acid is thrown down from the syrupy solution of tannic acid, in the form of a white powder (Guibourt).

The *luteogallic* acid of Guibourt here mentioned (which, according to him, exists together with ellagic acid in galls and bezoars) remains dissolved, whilst ellagate of potash is precipitated when a solution of the two acids in caustic potash is exposed to air containing carbonic acid. It is thrown down from the solution by hydrochloric acid, as an amorphous, dark-yellow precipitate, which cakes together on the filter to a resinous mass, insoluble in water, alcohol, and ether (Guibourt).

From Bezoars. Bezoars, freed from foreign substances and finely triturated, are placed in a vessel capable of being closed air-tight, which is then quite filled with a moderately strong solution of caustic potash, the quantities being so regulated that the ellagate of potash which is formed may not be deposited, while, at the same time, too great an excess of free potash is avoided. The vessel is now agitated to promote solution; the clear liquid (after standing) decanted; and a rapid stream of washed carbonic acid immediately passed through it, whereby ellagate of potash is thrown down, at first as a white, and afterwards as a green-grey precipitate. This is collected on a filter, washed several times with cold water, without stirring, and pressed between bibulous paper. From the alkaline filtrate hydrochloric acid throws down impure ellagic acid. The potash-salt is purified by crystallisation, to effect which it is dissolved in almost boiling water, which has been previously freed from air by boiling; the solution is filtered; the anhydrous (sometimes pale-green, sometimes yellow) salt left behind is dissolved by further addition of hot water; and the solution is set aside for some days, when bulky masses of delicate crystals are formed. These are collected on a filter, washed with cold water, pressed, and decomposed by dissolving them in hot water and pouring the solution into a moderate excess of dilute hydrochloric acid. The precipitated acid is washed with cold water and dried. Inasmuch as alkaline solutions of ellagic acid absorb oxygen rapidly from the air, and are altered, even in closed vessels, on long standing or by warming, the operations should be conducted as quickly as possible, and exposure to the air guarded against (Merklein & Wöhler).

Bezoars yield, by digestion in boiling alcohol and subsequent repeated boiling, a quantity of very pure ellagic acid, which crystallises on cooling; but much remains undissolved (Guibourt).

Properties. Crystallised ellagic acid heated to 200°—215°, is converted into the anhydrous acid, which, at a higher temperature, volatilises (especially in a stream of carbonic acid) partly undecomposed, without melting, and sublimes in delicate, sulphur-yellow needles; a large portion, however, is carbonised (Merklein & Wöhler. Braconnot. Ad. Göbel).

Anhydrous.			Pelouze.	Merklein Wöhler.	Ad. Göbel.	Rochleder & Schwartz
28 C 168	....	55·63	.... 55·22	.... 55·55	.... 55·38	... 55·38
6 H 6	....	1·99	.... 2·66	.... 2·13	.... 2·18	... 2·26
16 O 128	....	42·38	.... 42·12	.... 42·32	.... 42·44	.... 42·36
$C^{28}H^6O^{16}$.... 302	....	100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00

The acid of Pelouze and Rochleder & Schwartz was obtained from nutgalls, that of Merklein & Wohler and Göbel, from bezoars. — Pelouze gives the formula $C^7H^2O^4$; Merklein and Wöhler's formula $C^{14}H^3O^8$ requires to be doubled, on account of the uneven number of hydrogen-atoms.

Decompositions. 1. By heat (p. 185). —2. _Burns_ in the open fire without melting and without flame, emitting sparks (Braconnot). — 3. When ellagic acid is suspended in _water_ or _alcohol_, and the liquid evaporated, a dark-brown amorphous mass is formed (Ad. Göbel). — 4. _Hyponitric acid_ (Merklein & Wöhler) and warm _nitric acid_ (Braconnot) colour ellagic acid dark blood-red, with separation of red flakes : by prolonged action, oxalic acid and a small quantity of a bitter substance are produced (Braconnot). — The yellow- to green-brown solution in nitric acid of sp. gr. 1·13 to 1·35 is rendered yellow by water, and leaves, on evaporation, a yellow, hygroscopic mass. Nitric acid of sp. gr. 1·47 dissolves ellagic acid with red-brown colour ; on adding water, the solution becomes first red, then brownish, and lastly yellow ; cooled in snow for 12 or 16 hours, it throws down, after some days, bright, shining prisms soluble in water with transient red colour (Fr. Göbel). — 5. Ellagic acid is not perceptibly acted upon by _iodine_ (Braconnot) ; aqueous _iodic acid_ causes a copious evolution of carbonic acid, throws down iodine, and forms apparently the same amorphous, deliquescent, brown acid, which is produced by the prolonged action of air (Merklein & Wöhler). — 6. On mixing ellagate with _hypochlorite_ of potash, a salt of glaucomelanic acid is produced (Merklein & Wöhler). — 7. Ellagic acid, dissolved in excess of moderately dilute _caustic potash_ and exposed to the _air_, quickly assumes a deep red-yellow, almost blood-red colour, which becomes lighter on the formation of black crystals of glauco-melanate of potash (xv. 25) in the liquid (Merklein & Wöhler). It is not known what becomes of the carbon thereby liberated. — When ellagic acid is dissolved in a hot or a too strong solution (or in too little of a dilute solution) of caustic potash, the resulting glauco-melanate of potash is further converted into carbonate and oxalate of potash, and a salt of a soluble acid, which (after neutralising the solu-tion with acetic acid, and removing the oxalic acid by means of a lime-salt) produces a brown precipitate with neutral acetate of lead. By treating the lead-salt with hydrosulphuric acid, the hydrated acid may be obtained as an acid liquid drying up to a brown, deliquescent, amor-phous mass (Merklein & Wöhler). From ellagate of potash, which has become brown and amorphous from exposure to the air, acids throw down at first only ellagic acid, but after standing some days black-brown flakes are also precipitated (Ad. Göbel). On one occasion gallic acid was obtained on decomposing a solution of ellagic acid in caustic potash by means of hydrochloric acid (Pelouze). A similar reaction was observed also by Ph. Büchner (_Ann. Pharm._ 53, 186).

Combinations. — _With Water._ — _Crystallised ellagic acid._ Pale-yellow,

light powder, consisting of transparent, shining, microscopic prisms. In an impure state, greenish-brown (Merklein & Wöhler). By quick precipitation of the aqueous potash-salt with hydrochloric acid, pale yellow, very small prisms are obtained ; by slow decomposition of a very dilute solution at 60°, bright-yellow curved needles, having a silky lustre ; both appearing transparent under the microscope (Ad. Göbel). — Specific gravity 1·667 at 18°. Tasteless. Has a weak acid reaction (Merklein and Wöhler).

Loses, when heated. 11·7 p. c. water (Pelouze), on an average 10·88 p. c. (Merklein & Wöhler) (4 at. = 10·64 p. c. HO). A part of this water is given off at 100°, and is taken up again from the air by the acid dried at 120°, but not by that completely dried at 200° (Merklein & Wöhler). The acid dried at 120° is $C^{28}H^6O^{15} + 2HO$ (Ad. Göbel).

		at 120°.				Ad. Göbel.
28	C	168		52·5		52·24
8	H	8		2·5		2·41
18	O	144		45·0		45·35
$C^{28}H^6O^{15}$ + 2aq.		320		100·0		100 00

Ellagic acid is but slightly soluble in boiling *water*. *Oil of vitriol* poured upon it colours it lemon-yellow, and when gently heated dissolves it, forming a yellow solution, from which the crystallised acid is precipitated unaltered on addition or absorption of water (Merklein & Wöhler). Even after the solution in oil of vitriol has been heated to 140°, the acid is thrown down by water, unchanged (Robiquet, *J. pr. Chem.* 8, 124).

Ellagic acid is *bibasic*. Its salts $C^{28}H^4M^2O^{16}$ are easily decomposible in the moist state. The precipitates thrown down by aqueous ellagate of potash from salts of the earths and heavy metals are yellow or brown, and distinguishable under the microscope as mixtures of amorphous granules, flakes, crystals of the new compound, and needles of separated ellagic acid. On heating the acid with baryta- or lime-water, or hydrate of magnesia, and washing with water (free from carbonic acid), alcohol, and ether, a leek-green baryta-salt, a dirty dark yellow lime-salt, or a pale-yellow magnesia-salt, is obtained, seen, under the microscope, to consist of delicate, pellucid grains and prisms, insoluble in cold and in boiling water (Ad. Göbel).

Ellagate of Ammonia. — Ellagic acid dissolves but slightly in aqueous solution of ammonia, but absorbs the ammonia therefrom (Braconnot, Merklein & Wöhler). — A solution of di-ellagate of soda, mixed with sal-ammoniac, yields the ammonia-salt as a pale olive-green precipitate, without liberating free ammonia. Crystallised ellagic acid absorbs gaseous ammonia, and is converted, with loss of water, but without any great alteration of weight, into the ammonia-salt. From 100 parts of dry acid, 113·1 parts of greenish-yellow ammonia-salt are obtained ($C^{28}H^6O^{16}$,?NH³ = 111·2) a considerable amount of heat being developed in the formation (Merklein and Wöhler).

Ellagate of Potash. — Ellagic acid dissolves freely in caustic potash, with deep yellow colour. Carbonic acid throws down from the solution a basic potash-salt (Merklein & Wöhler) which is decomposed by re-

crystallisation from water, more difficultly soluble salts being formed, in which the proportion of potash is diminished, while that of the acid is increased (Ad. Göbel). The moist potash-salts are easily decomposed by carbonic acid and by air (see above).

a. *With* 3 *at. Potash.* When ellagic acid or di-ellagate of potash is treated with alcoholic potash, a deep lemon-yellow powder is obtained, consisting of microscopic, yellow, transparent prisms. After washing with alcohol (without exposure to the air), pressing, and drying in a vacuum over oil of vitriol, the salt contains 34 p. c. potash, and may be represented by the formula $C^{28}H^4K^2O^{16},KO$. (By calc. 33·2 p. c. KO). On exposure to the air, it assumes a black-green colour, and is converted into a mixture of di-ellagate and carbonate. Dissolves readily in water, but not in alcohol (Merklein & Wöhler).

b. *Di-ellagate.* — *Preparation* (p. 187). The salt, if washed with water alone, rapidly decomposes on drying; it must, therefore, be washed with water, alcohol, and ether, in succession, and dried at a temperature of 30—40°, after which treatment, little or no alteration takes place (Ad. Göbel). Very light, loose, paper-like mass, consisting of long, microscopic prisms, generally greenish-grey or greenish-yellow from slight decomposition, and more rarely of a pale-yellow colour. Hydrated, but rendered anhydrous and yellow by boiling in its saturated solution. Glows when heated, without giving off odorous products. Dissolves slightly in cold, abundantly in hot water, with greenish-yellow colour (Merklein & Wöhler). Neutral (Ad. Göbel).

		at 100—215°.		Merklein & Wöhler.		Ad. Göbel.
28	C	168	....	44·39 .... 44·28	..	45·16
4	H	4	....	1·06 .... 1·33	....	1·16
14	O	112	..	29·59 .... 29·91	....	29·35
2	KO	94·4	..	24·96 ... 24·48	...	24·33

$C^{28}H^4K^2O^{16}$ .... 378·4 .... 100·00 .... 100·00 .... 100·00

Ad. Göbel describes another salt, obtained in the same manner as b, containing 28·94 p. c. potash. By recrystallisation of b he obtained a dark-green, delicately crystallised salt, which, at 215°, contained 45·28 p. c. C, 1·16 H, 32·58 O, and 20·98 KO, corresponding to the formula $3C^{28}H^4O^{14},5KO + HO$ (calc. 45·96 p. c. C, 1·18 H, 31·38 O, and 21.48 KO).

Ellagate of Soda. a. *With* 3 *at. Soda?* — The deep-yellow solution of ellagic acid in boiling caustic soda, cooled out of contact with air, throws down a bulky precipitate of fine lemon-yellow nodules, readily soluble in water, and blackening easily. — b. *Di-acid.* Precipitated from the same solution by carbonic acid as a bright-yellow, crystalline powder, containing 17·3 p. c. soda ($C^{28}H^4Na^2O^{16}$ = 17·99 p. c. NaO). More difficultly soluble than the potash-salt (Merklein & Wöhler).

Ellagate of Baryta. — By digestion in baryta-water, ellagic acid is coloured deep lemon-yellow, without being dissolved. The salt thereby formed absorbs carbonic acid from the air, and assumes a dark pistachio-green colour; it contains, at 140°, 45·35 p. c. baryta,

indicating the formula $C^{28}H^4O^{14},3BaO$ (calc. 44·6 p. c. BaO) (Merklein & Wöhler).

Ellagate of Lime behaves like the baryta-salt. — Ellagic acid takes up the whole of the lime from lime-water.

With solution of *sesqui-chloride of iron*, ellagic acid forms a greenish liquid, changing to black-blue, like ink, without throwing down a precipitate ; sulphurous acid, added to the mixture, converts it into a jelly, which afterwards becomes fluid and loses its colour, while crystalline ellagic acid is separated. Heated with alcoholic sesqui-chloride of iron, the acid swells up to a bulky, deep-blue mass, which, after drying, is black and insoluble in water, and by treatment with hydrochloric acid, yields ferroso-ferric oxide, with separation of ellagic acid (Merklein & Wöhler).

Ellagate of Lead. — On mixing alcoholic ellagic acid with an alcoholic solution of neutral acetate of lead, a yellow, amorphous precipitate is produced, which is dark olive-green when dry. Contains 63 p. c. oxide of lead ($C^{28}H^4Pb^2O^{16} = 61$ p. c. PbO) (Merklein & Wöhler).

Ellagic acid is slightly soluble in *alcohol*, insoluble in *ether* (Merklein & Wöhler).

Primary Nucleus $C^{28}H^{18}$; *Oxygen-nucleus* $C^{28}H^{10}O^8$.

Morindone.

$$C^{28}H^{10}O^{10} = C^{28}H^{10}O^8,O^2.$$
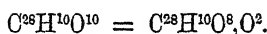
ANDERSON. *Chem. Gaz.* 1848, 313 ; *Ann. Pharm.* 71, 323 ; *J. pr. Chem.* 47, 437 ; *N. J. Pharm.* 18, 249.

Obtained, by sublimation of morindin, in the form of microscopic, long, four-sided needles with oblique end-faces, of an exceedingly rich and beautiful red colour. The needles are washed with water, and dried at 100°.

					Anderson.
28 C	168	....	65·12	....	65·81
10 H	10	....	3·87	....	4·18
10 O	80	....	31·01	....	30·01
$C^{28}H^{10}O^{10}$	258	..... .	100·00	....	100·00

The formula is doubtful. Perhaps identical with alizarin (xiv, 129) (Rochleder, *Wien. Akad. Ber.* 7, 806). Isomeric with gentianic acid (p. 178).

Insoluble in *water*, whether cold or hot. — Dissolves in *oil of vitriol*, with fine violet colour, and is precipitated by water. —Soluble in *alkalis*, with splendid violet colour. The ammoniacal solution precipitates *baryta-water* cobalt-blue, *solution of alum* red.

Dissolves readily in *alcohol* and in *ether*, crystallising on evaporation.

Morindone dyes cloth prepared with alum-mordant deep rose-red ; with iron-salts, violet and black ; the colours are not stable.

Morindin.

$C^{28}H^{15}O^{15}$?
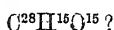
ANDERSON.   *Trans. Roy. Soc. Edinb.* 16, 435; *Chem. Gaz.* 1848, 313; *Compt. chim.* 1849, 35; *N. J. Pharm.* 18, 249; *Ann. Pharm.* 71, 216; *J. pr. Chem.* 47, 431.

The yellow colouring matter of the root of *Morinda citrifolia* (*Handbuch* viii. *Phytochem.* 56).

Preparation. The bark of the root is boiled with six times its weight of alcohol, and the tincture filtered boiling hot; morindin, mixed with red colouring matter, is then thrown down on cooling. By repeated boiling of the bark in alcohol, a further quantity of purer morindin is obtained. It is crystallised several times from alcohol of 50 p. c., and afterwards (to remove a little ash with which it is contaminated) from alcohol containing a small quantity of hydrochloric acid.

Properties. Sulphur-yellow, delicate needles, having a silky lustre. Separates on cooling, from a solution in boiling water, in the form of a jelly.

		at 100°.			Anderson.
28	C	168	....	55·44	...... 55·43
15	H	15	......	4·95	.... 5·11
15	O	120	....	39·61	...... 39·16
	$C^{28}H^{15}O^{15}$	303	....	100·00	.... 10·000

Probably identical with ruberythric acid (p. 42) (Rochleder, *Wien. Akad. Ber.* 7, 806).

Decompositions. When *heated* it melts to a dark-brown liquid, boils, and gives off orange-coloured vapours of morindone, which condense to red needles, whilst carbon is left behind. Dissolves in *oil of vitriol*, forming a purple solution, from which water precipitates, after standing some time, yellow flakes of a substance soluble in ammonia with violet colour, probably morindone. — *Nitric acid* of sp. gr. 1·38 dissolves it with deep brown-red colour; the solution loses its colour when heated, giving off red vapours, and does not contain any oxalic acid even after boiling.

Combinations. Slightly soluble in cold, easily in boiling *water*, forming a yellow solution (see above). Dissolves in aqueous *alkalis* with orange-red colour. — Precipitates solutions of *baryta-, strontia-,* and *lime-salts* red; solution of *alum* of a reddish colour. *Sesquichloride of iron* is coloured by the alcoholic solution of morindin deep-brown without precipitation; with the ammoniacal solution it produces a brown lake. — Solutions of morindin precipitate *neutral acetate of lead* in scarlet flakes which give up colouring matter to water.
Slightly soluble in cold absolute, abundantly in boiling dilute *alcohol.* Insoluble in *ether.* — Dyes cloth mordanted for Turkey-red a permanent red-brown.

Primary Nucleus $C^{28}H^{24}$; *Oxygen-nucleus* $C^{28}H^{18}O^6$.

Mayna-resin.

$$C^{28}H^{18}O^8 = C^{28}H^{18}O^6,O^2?$$
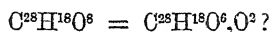
Lewy. *Compt. rend.* 18, 242; *N. Ann. Chim. Phys.* 10, 374; abstr. *Ann. Pharm.* 52, 404.

The resin which exudes from incisions made in the trunk of *Cholophyllum caloba* or *Ch. longifolium*, a tree growing principally in the American province Maynas. Crystallises from boiling alcohol.

Properties. Fine yellow prisms belonging to the oblique prismatic system. Combinations of the rhombic prism *u* with the perpendicular truncation-faces *m* and *t* (Fig. 97), the four octahedral faces *h*, and the oblique end-face *f* and clinodome *α* belonging thereto (Fig. 99). $u : m = 119°$; $u : α = 98° 45'$ (nearly); $t : f = 139° 35'$; $t : u = 150° 30'$ (De la Provostaye). Sp. gr. 1·12. Melts at 105° to a transparent glass which solidifies again at about 90°.

					Lewy.
					mean.
28 O	168		67·20		67·47
18 H	18		7·20		7·30
8 O	64		25·60		25·23
$C^{28}H^{18}O^8$	250		100·00		100·00

Yields, by *dry distillation*, an empyreumatic oil, and leaves charcoal. — Slowly attacked by *bromine* and *chlorine*. Warm *nitric acid* of sp. gr. 1·33 decomposes it, with copious evolution of red vapours and formation of butyric and oxalic acids, and crystals of a substance which is soluble in water and does not precipitate lime-salts. Fuming nitric acid dissolves it, with violent reaction; water throws down from the solution a yellow, amorphous acid soluble in alcohol and in ether. — Heated with sulphuric acid and *bichromate of potash*, it evolves carbonic and formic acids.

Insoluble in *water.* — Dissolves in *oil of vitriol* with fine red colour; water precipitates it unchanged. — Readily soluble in *ammonia*, and in aqueous *alkalis.*— *Nitrate of silver* precipitates from the ammoniacal solution (freed from excess of ammonia) a silver-salt of variable composition.

Dissolves easily in *alcohol, ether, acetic acid*, and in *oils*, both *fixed* and *volatile*.

Oxygen-nucleus $C^{28}H^{16}O^8$.

Physalin.

$$C^{28}H^{16}O^{10} = C^{28}H^{16}O^8,O^2.$$
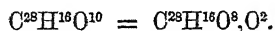
Dessaignes & Chautard. *N. J. Pharm.* 21, 24; *N. Repert.* 1, 216; *J. pr. Chem.* 55, 323,

The bitter principle of *Physalis Alkekengi* (*Handbuch*, viii. *Phytochem.* 59).

Preparation. The leaves of the plant are exhausted with cold water, and the infusion is shaken for ten minutes with chloroform, in the proportion of 20 grammes chloroform to a litre of the liquid. After separation has taken place, the aqueous liquid is decanted and again shaken with chloroform in the same proportion. The chloroform is allowed to evaporate, the residue dissolved in hot alcohol, and the solution shaken with animal charcoal and filtered. The physalin is precipitated from the filtrate by water, and washed.

Light, white, or slightly yellow powder, becoming electric when rubbed; not crystalline under the microscope. Taste, at first slight, afterwards persistently bitter.

			Dried in vacuo.		Dessaignes & Chautard. mean.
28 C	....	168	......	63·64	.... . 63·67
16 H	.. ..	16	....	6 06	.... 6·31
10 O	....	80	....	30 30	..... 30·02
$C^{28}H^{16}O^{10}$	....	264	... ..	100·00	..... 100 00

Becomes soft at 180°, of a pasty consistence at 190°, and at a higher temperature is coloured, froths up and burns, without leaving any residue.

Dissolves very slightly in cold, and rather more freely in hot *water*. — Very little soluble in dilute *acids*, with which it does not combine. — Dissolves readily in aqueous *ammonia*, and is left unaltered on evaporation.

An alcoholic solution of physalin added to ammoniacal *neutral acetate of lead* throws down yellow flakes, which, after being washed and dried in a vacuum, contain 54·34 p. c. oxide of lead, and are probably $C^{28}H^{15}O^9,3PbO$ (calc. 56·70 p. c. PbO).

Not precipitated from its alcoholic solution by ammoniacal *nitrate of silver*.

Dissolves freely in *alcohol* and in *chloroform*, slightly in *ether*.

Gentiogenin.

$$C^{28}H^{16}O^{10} = C^{28}H^{16}O^8,O^2.$$
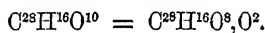
Kromayer.   *N. Br. Arch.* 110, 37.

Obtained, together with fermentable sugar, by boiling gentian-bitter with dilute acids.

Gentian-bitter, dissolved in about 4 times its weight of water, is heated in the water-bath for a quarter of an hour with dilute hydrochloric acid; the product, when cold, is diluted with water, which throws down the gentiogenin in yellowish-brown flakes. An additional quantity may be obtained by boiling down the filtrate, extracting the residue with alcohol, concentrating the alcoholic extract, and precipitating with water. — When gentian-bitter is boiled for a longer

time with dilute acids, only a small quantity of gentiogenin is obtained, probably because the greater portion is converted into a substance soluble in water.

Amorphous, yellowish-brown powder, having a bitter taste. Permanent in the air. Neutral.

		at 100°.		Kromayer.
28 C	168	63·64		63·10
16 H	16	6·06		6·93
10 O	80	30·30		29·97
$C^{28}H^{16}O^{10}$	264	100·00		100·00

Heated on platinum-foil, it melts and burns. — It reduces boiling ammoniacal *nitrate of silver*.

Gentiogenin which has been dried in the air, loses 7·02 p. c. water at 100° (2 at. = 6·38 p. c.). It dissolves slightly in cold *water*, and cakes together to a resinous mass in boiling water.

Soluble in strong *mineral acids* and in aqueous *alkalis*, forming brown solutions. — Not decomposed by *sesquichloride of iron*, nor precipitated by *lead-salts*.

Easily soluble in *alcohol;* moderately soluble in *ether-alcohol.*

Gentian-bitter.

$$C^{40}H^{30}O^{24} ?$$
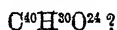
Kromayer. *Die Bitterstoffe.* Erlangen 1861, 105. — *N. Br. Arch.* 110, 27.

Gentianin. Gentiopicrin. — The bitter principle of the root of *Gentiana lutea* (*Handbuch,* viii, *Phytochem,* 58), formerly confounded with gentianic acid (p. 178). Obtained impure and in the form of extract by Bracon not (*J. Phys.* 84, 347), Dulk (*N. Br. Arch.* 15, 225; *Berz. Jahresber.* 19, 552), Leconte (*J. Pharm.* 23, 467), Mouchon (*Pharm. Viertelj.* 8, 133), and Leibundgut (*N. Br. Arch.* 107, 132), and in the pure state by Kromayer.

Preparation. From the *fresh* roots: the dried roots do not yield the crystalline bitter. The roots, washed with cold water and cut into small pieces, are exhausted twice with warm alcohol of 70°; a tincture is thus obtained, from which the greater part of the alcohol is removed by distillation, and the residue is reduced to $\frac{1}{12}$th of the root employed. This is then mixed with 3 volumes of water, and treated twice with granulated animal charcoal, which collects and retains nearly the whole of the gentian-bitter. The charcoal (after being washed with cold water till the water is no longer coloured) is dried at a gentle heat and boiled with alcohol of 80°; the alcoholic extract is again freed from alcohol by distillation; and the residue is diluted with water, and filtered to remove the resin thereby thrown down. The filtrate is now heated for some hours in a water-bath with levigated oxide of lead; the product is diluted with water and filtered hot; the lead is removed by precipitating with hydrosulphuric acid and filtering the still hot liquid; and the

pale-brown filtrate is evaporated to a syrup and shaken up with ether. On being left to itself for a day, the mixture solidifies to a crystalline mass, which is pressed, and re-crystallised from a small quantity of hot water, with the aid of a little charcoal. — A part of the gentian-bitter remains in solution when the aqueous extract is heated with animal charcoal. To recover it, the solution is precipitated with basic acetate of lead, filtered, the filtrate freed from lead by hydrosulphuric acid, and evaporated to a syrup. The syrup is dissolved in alcohol, afterwards mixed with ether (which separates the sugar), and the ether-alcoholic solution is concentrated to a syrup. This is then shaken up with ether, and the resulting crystalline mass purified as above. — Six pounds of fresh roots yield 4 grammes of gentian-bitter.

Properties. Hydrated crystallised gentian-bitter (see below) is rendered anhydrous by heating to 100°. Melts at 120—125° to a brown liquid, solidifying, on cooling, to an amorphous, brown mass, which forms a white powder when triturated. Taste, intense and pure bitter. Neutral. Does not contain nitrogen.

		at 100°.		Kromayer.
40 C	240	51·95	52·03
30 H	30	6·49	6·47
24 O	192	41·56	41·50
C⁴⁰H³⁰O²⁴	462	100·00	100 00

The correctness of the formula is doubtful.   (Kr.)

Decompositions. 1. *Heated* on platinum-foil, it turns brown, smelling like caramel, and burns without leaving a residue. — 2. The colourless solution in strong *nitric acid* turns brown when heated, and, on addition of water, throws down yellow flakes; on boiling the solution, oxalic acid is produced. — 3. *Oil of vitriol* dissolves gentian-bitter, forming a colourless solution, which, on gentle heating, assumes a magnificent carmine-red colour; water precipitates it in grey flakes. — 4. Decomposed by boiling with *dilute sulphuric acid*, or *hydrochloric acid*, with separation of yellow flakes of gentiogenin, and formation of fermentable sugar. The same decomposition is effected by oxalic and acetic acids, but not by beer-yeast. C⁴⁰H³⁰O²⁴ = C²⁸H¹⁶O¹⁰ + C¹²H¹²O¹² + 2HO. From 100 parts dry gentian-bitter, 31·9, 33·8, and 40·2 parts sugar were obtained (calc. 38·9 p. c. C¹²H¹²O¹²). — 5. Gentian-bitter is not altered by *sesquichloride of iron*, and does not throw down cuprous oxide from a solution of cupric oxide containing caustic potash. It reduces boiling ammoniacal *nitrate of silver*.

Combinations. — *With Water.* — *Crystallised Gentian-bitter.* Radiated groups of colourless needles, which, on exposure to the air, become covered with a white crust. Loses, on an average, 2·56 p. c. water at 100°, corresponding (in the uneffloresced crystals) to 1½ (calc. = 2·83 p c. HO), or perhaps 2 atoms.

Dissolves readily in water, and crystallises from a syrupy solution, on standing in a warm place.

Dissolves in cold aqueous *ammonia*, without colour; in warm ammonia it assumes a yellow colour, which does not disappear on the

addition of acids. — Solutions of caustic *potash* and *soda* dissolve it with yellow colour.

Soluble in cold *alcohol* containing water; in absolute alcohol only when heated. Insoluble in *ether*.

Primary Nucleus $C^{28}H^{26}$; *Oxygen-nucleus* $C^{28}H^{24}O^2$.

Lichenic Acid.

? $C^{28}H^{24}O^6 = C^{28}H^{24}O^2,O^4.$

SCHNEDERMAN & KNOP. *Ann. Pharm.* 55, 149—150; *J. pr. Chem.* 36, 117; *Pharm. Centr.* 1845, 858.

Lichenstearic acid.

Sources. In *Cetraria islandica* (*Handb.* viii., *Phytochem.* 96) (Schnederman & Knop). An acid agreeing in properties with lichenic acid is found in toadstools (*Agaricus muscarius, Handb.* viii., *Phytochem.* 98); it is precipitated from an alcoholic solution of the extract by water (Bolley, *Ann. Pharm.* 86, 50).

Preparation. Iceland moss is boiled for a quarter of an hour in alcohol containing carbonate of potash. To the strained decoction an excess of hydrochloric acid is added, and the whole is diluted with 4 or 5 volumes of water. The precipitate thereby formed is washed with water, and afterwards boiled three or four times with alcohol of 42 to 45 p. c. On cooling the alcoholic solution, a mixture of lichenic and cetraric acids, with a third substance, is separated, from which the lichenic acid is taken up by boiling rock-oil, and again deposited on cooling, or more completely on partial distillation. Purification is effected by recrystallising from alcohol with the help of animal charcoal.

Properties. Loose, white mass, consisting of delicate crystalline laminæ having a pearly lustre. From a solution in very dilute alcohol it is obtained in small rhombic tables; on concentrating the solution, partly in oily drops. — Inodorous. Has a rancid, harsh taste, not bitter. Melts at about 120° without loss of weight, and solidifies to a crystalline mass. Not volatile. Contains no nitrogen.

				Schnederman & Knop. *mean.*
28 C	168	70		70·44
24 H	24	10		10·08
6 O	48	20		19·48
$C^{28}H^{24}O^6$	240	100		100·00

The above is Strecker's formula (*Ann. Pharm.* 67, 54); Schnederman & Knop give $C^{29}H^{25}O^6$.

Perfectly insoluble in *water*.

The *salts* of lichenic acid are permanent in the air, and are decomposed by acids, with separation of lichenic acid. Their solutions froth up on boiling.

Lichenate of Ammonia. — The easily prepared solution of the acid in warm aqueous ammonia forms, on cooling, a white, elastic jelly, seen under the microscope to contain a quantity of long, extremely delicate crystals. The salt, when dry, is white and silky, and only partially soluble in warm water, with loss of ammonia.

Lichenate of Potash. — A solution of the acid in aqueous carbonate of potash throws down, when concentrated by evaporation, yellowish flakes, which are soluble in water, but insoluble in alkaline liquids. If the solution be evaporated to dryness, and the residue extracted with boiling absolute alcohol, a part of the salt is obtained, on cooling, as an indistinctly crystalline powder; and the remainder, on concentrating the solution, in the form of a syrup. — Dissolves easily in water, forming an alkaline liquid, which tastes like soap, and froths up on boiling.

Lichenate of Soda. — Obtained in the same manner as the potash-salt. A concentrated aqueous solution throws down white granules on standing.

Lichenate of Baryta. — Obtained, on precipitating aqueous lichenate of soda with a soluble baryta-salt, as a greyish-white precipitate, which cakes together in boiling water.

		Dried over the water-bath.			Schnederman & Knop.
28	C	168	.. ..	54·63	54·95
23	H	23	....	7·48	7·53
5	O	40	....	13·34	12·76
	BaO	76·5	.. ..	24·55	24·76
	C²⁸H²³BaO⁶	307·5	....	100·00	100·00

Lichenate of Lead. — Neutral acetate of lead precipitates the aqueous soda-salt in white flakes, which, on boiling the liquid, melt to a yellow, semi-fluid mass. — Brittle, softening between the fingers, and becoming semi-fluid at 100°. Appears to undergo decomposition at 100°.

					Schnederman & Knop.
28	C	168	....	49·01	49·50
23	H	23	....	6·71	6·87
5	O	40	....	11·67	11·54
	PbO	112	....	32·61	32·09
	C²⁸H²³PbO⁶	343	....	100·00	100·00

Lichenate of Silver. — Thrown down, from a solution of the soda-salt, by nitrate of silver, as a greyish-white precipitate, turning violet on exposure to light, and caking together in boiling water. —Decomposes below 100°.

	Air-dried.			Schnederman & Knop.
C²⁸H²³O⁵	231	....	66·55	68·16
AgO	116	.... ..	33·45	31·84
C²⁸H²³AgO⁶	347	....	100·00	100·00

Lichenic acid dissolves readily in *alcohol*, in *ether*, and in *volatile* and *fixed oils.*

Oxygen-nucleus $C^{28}H^{18}O^8$.

Olivil.

$$C^{28}H^{18}O^{10} = C^{28}H^{18}O^8,O^2.$$

PELLETIER. *Ann. Chim. Phys.* 3, 105; *J. Pharm.* 2, 336. — *Ann. Chim. Phys.* 51, 196; *Schw.* 67, 91; *Ann. Pharm,* 6, 31.
SOBRERO. *N. J. Pharm.* 3, 286; *J. pr. Chem.* 29, 479. — *Ann. Pharm.* 54, 67.

Olivile.—Discovered by Pelletier in 1816.

Sources. Occurs, together with resin and a little benzoic acid, in the gum of the olive tree (*Handb.* viii., *Phytochem.* 47) (Pelletier). The gum of this tree contains, besides olivil, a resin soluble in ether and in hot alcohol, a second resin little soluble in ether, but easily soluble in hot and cold alcohol, and a gum insoluble in both liquids (Sobrero). See also Tromsdorff on the resin of the olive tree (*N. Tr.* 19, 2, 42).

By exhausting olive leaves with dilute hydrochloric acid, precipitating the concentrated extract with ammonia, dissolving the precipitate in dilute hydrochloric acid, and precipitating with magnesia, Landerer (*Repert.* 57, 205) obtained a precipitate which, when treated with alcohol, yielded crystals having a bitter, disagreeable taste, insoluble in alcohol, but soluble in dilute acids, without forming with them crystallisable compounds. Crystals were also obtained by treating an alcoholic extract of fresh olive-leaves with dilute acetic acid, precipitating the solution with neutral acetate of lead, freeing the filtrate from lead by means of hydrosulphuric acid, and evaporating. These crystals were deliquescent, and melted when heated in a platinum spoon, giving off an aromatic odour, and leaving a residue of charcoal. — Landerer (*Repert.* 72, 348) afterwards obtained crystals from unripe olives, but did not further examine them.

Preparation. The finely powdered gum is digested with ether to remove the resin, and the residue is boiled with alcohol of 36°. The quickly-filtered solution solidifies to a crystalline mass, which is purified by washing with cold alcohol and re-crystallising from a boiling alcoholic solution (Pelletier, Sobrero).

Properties. Obtained from absolute alcohol in anhydrous crystals, at 118 — 120°, which melt to a transparent liquid without loss of weight. The melted mass solidifies, on cooling, to a colourless or yellowish transparent resin, which cracks, and, when powdered, becomes electric; heated to 70°, it again becomes fluid, but crystallises from alcohol in its original state.—Inodorous, tastes bitter-sweet, somewhat aromatic. Neutral.

		Fused.				Sobrero.
28 C	....	168	....	63·15	....	63 42
18 H	....	18	....	6 79	....	6·81
10 O	....	80	....	30·06	....	29·77
$C^{28}H^{18}O^{10}$	....	266	....	100 00	....	100·00

Pelletier found (in anhydrous olivil ?) 61·47 p. c. C., and 8·06 H.; he gave the formula $C^{12}H^9O^4$.

Decompositions. Olivil subjected to *dry distillation* melts and puffs up, giving off water (acetic acid, according to Pelletier) and pyrolivilic acid (xiv, 206), whilst a black pasty mass, partially soluble in alcohol, remains behind. By prolonged heating, other volatile products, differing from pyrolivilic acid, are obtained, till at last charcoal remains (Sobrero). — 2. *Burns* with white flame, and leaves a large quantity of porous charcoal. — 3. *Chlorine*, passed into aqueous olivil, throws down brown flakes containing chlorine, which are afterwards decomposed, with evolution of carbonic acid. — 4. *Oil of vitriol* colours olivil blood-red, and then carbonises it; in a moderately dilute aqueous solution of olivil it precipitates olivirutin. — 5. Dry olivil absorbs *hydrochloric acid gas*, becoming transparent and green, and, on heating, is converted into olivirutin. From the pale-green solution in cold fuming hydrochloric acid, water precipitates unchanged olivil, but after heating, it separates olivirutin. — 6. *Strong nitric acid* attacks it violently, with abundant evolution of hyponitric acid. With nitric acid diluted with its own volume of water, it forms a deep red-yellow solution, which, when heated, becomes nearly colourless, evolving scarcely any red fumes, but much hydrocyanic acid, and contains, after the reaction, a large quantity of oxalic acid.— Very weak nitric acid colours aqueous olivil reddish-yellow. — 7. A solution of olivil in *caustic potash* assumes a yellowish-green, afterwards a brown colour, more especially, as it seems, on exposure to the air. — 8. *Chromic acid* and bichromate of potash precipitate aqueous olivil in brown flakes, which soon become green and granulated. No gas is evolved in the reaction. The precipitate, collected after several times boiling the solutions, and washed with boiling water and alcohol, loses, at 150°, the whole of its water, is uncrystallisable, and contains 44·90 p. c. C., 4·33 H., 29·27 O., and 21·50 Cr²O³, nearly corresponding to the formula $C^{28}H^{18}O^{13},Cr^2O^3$. — 9. *Peroxide of lead* is decolorised by boiling with aqueous olivil, without evolution of gas, and, after some days' boiling, is converted into a light powder containing oxide of lead and a resinous oxidation-product of olivil. — 10. Aqueous olivil colours *sulphate of copper*, on boiling, pale-green; it immediately reduces *gold* and *silver-salts* (Sobrero).

Combinations. — *With Water.* — A. *With 1 at. Water.* Olivil crystallised from water and dried in a vacuum, loses, when melted, from 2·56 to 3·33 p. c. water (1 at. = 3·27 p. c. HO) (Sobrero).

		In vacuo.			Sobrero. mean.
28 C	....	168	....	61·09	.... 61·01
19 H	....	19	....	6·90	.... 7·08
11 O	....	88	....	32·01	.... 31·91
$C^{28}H^{18}O^{10}$ + Aq.	....	275	. .....	100·00	.... 100·00

B. *With 2 at. Water.* — Colourless, transparent prisms, grouped in stars. They lose from 5·95 to 6·17 p. c. water when fused (2 at. = 6·33 p. c. HO) (Sobrero).

C. *Aqueous solution.* — Olivil dissolves in water, especially when hot (Sobrero), in 32 parts boiling water (Pelletier). In a quantity of

water not sufficient for complete solution, it melts at 70° to an oily liquid, solidifying to a crystalline mass on cooling. It is not altered by prolonged boiling with water. A hot aqueous solution of olivil containing resin, grows turbid on cooling, and becomes clear again only after long standing, forming, at the same time, a granular deposit (Sobrero).

Olivil crystallises unchanged from dilute *sulphuric* and *hydrochloric acids.* — It does not decompose *alkaline carbonates* (Sobrero), but dissolves in aqueous *ammonia, potash,* and *soda* (Pelletier), and is precipitated unaltered by acetic acid (Sobrero).

Lead-compound. — Neutral acetate of lead throws down from aqueous olivil white flakes, insoluble in acetic acid (Pelletier). When aqueous olivil is precipitated by basic acetate of lead, salts containing from 47·07 to 55·40 p. c. oxide of lead are obtained, the last of which may perhaps be represented by the formula $C^{28}H^{18}O^{10},3PbO$ (calc. = 55·70 p. c. PbO) (Sobrero). — An aqueous solution of nitrate of lead, added to a large excess of aqueous olivil and ammonia, throws down a precipitate containing a smaller proportion of oxide of lead. In this case also, the salt varies in composition (Sobrero).

		at 130°.				Sobrero. mean.
28	C	168	....	34·29	... .	34·39
18	H	18	... ...	3·68	....	3·54
10	O	80	....	16·32	... .	16·46
2	PbO	224	....	45·71	....	45·61
$C^{28}H^{18}O^{10},2PbO$		490	....	100·00	....	100·00

Olivil dissolves in *wood-spirit* and in *alcohol.* Boiling alcohol dissolves it in all proportions ; it is thrown down from a moderately dilute solution on cooling in crystals ; whilst, from a concentrated and resinous solution, starch-like granules are deposited (Pelletier, Sobrero).

It dissolves slightly in *ether,* and freely in strong *acetic acid,* from which it is not precipitated by water. Soluble, according to Sobrero, in *volatile* and *fixed oils ;* according to Pelletier, only in small quantity, separating again on cooling.

Appendix to Olivil.

Olivirutin.

SOBRERO. *Ann. Pharm.* 54, 80.

Formation and Preparation. 1. When oil of vitriol is added to aqueous olivil, a precipitate is produced consisting first of pale, and afterwards of dark red flakes, which dissolve, on further addition of oil of vitriol, and are again precipitated by water. — 2. Dry hydrochloric acid gas is passed over olivil, and the temperature gradually raised to 100°, whereupon the green substance first formed turns red, and on washing with water leaves olivirutin. — 3. Olivil is dissolved in fuming hydrochloric acid and heated for some time in the water-bath, when a thick, dark-red precipitate of olivirutin is produced.

Olivirutin forms a sometimes rose-red, sometimes dark-red powder, varying slightly in colour and composition according to the temperature at which it is produced, and the strength of the acids employed.

	By oil of vitriol. mean.	By hydrochloric acid. Bright-red.	Dark-red.
C	68·60	67·96	69·14
H	6·38	6·19	5·92
O	25·02	25·85	24·94
	100·00	100·00	100·00

Differs from olivil in containing a smaller proportion of the elements of water (Sobrero).

Decomposed by *heat*, giving off the peculiar odour which is produced by olivil.

Insoluble in *water*; soluble in aqueous *ammonia* with fine violet-red colour. — The alcoholic solution precipitates *basic acetate of lead*, and, after addition of ammonia, likewise precipitates *baryta*- and *lime-salts*; it precipitates alcoholic *acetate of copper* after some time.

Dissolves in *alcohol*, and is precipitated from the solution by water.

Oxygen-nucleus $C^{28}H^{16}O^{10}$.

Cyclamiretin.

$$? \; C^{28}H^{16}O^{12} = C^{28}H^{16}O^{10},O^2.$$
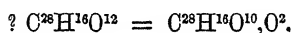
TH. MARTIUS. *N. Repert.* 8, 395.

Produced, together with grape-sugar, on boiling cyclamin wit dilute acids; it is thrown down as a white granulated precipitate.

Resinous. Easily soluble in alcohol; insoluble in water and ether.

Glucoside of Cyclamiretin.

Cyclamin.

$$C^{40}H^{24}O^{20} = C^{28}H^{14}O^{10},C^{12}H^{10}O^{10} \; ?$$

SALADIN. *J. chim. méd.* 6, 417; *Br. Arch.* 31, 245.
BUCHNER & HERBERGER. *Repert.* 37, 36.
DE LUCA. *Cimento* 5, 225; *Compt. rend.* 44, 723; *N. J. Pharm,* 31, 427; *J. pr. Chem.* 71, 330; *N. Br. Arch.* 94, 60. — *Cimento* 8, 182; *Compt. rend.* 47, 295 and 328; *N. J. Pharm.* 34, 353.
TH. W. C. MARTIUS. *N. Repert.* 8, 388.

Arthanitin (Saladin.) — The poisonous constituent of the tuberose roots of *Cyclamen europœum* (*Handb.* viii, *Phytochem.* 63). Occurs in small quantity in the root of *Primula veris*, and in still smaller quantity in the roots of *Limosella* and *Anagallis* (Saladin).

Landerer (*Repert.* 58, 111) by distilling freshly bruised cyclamen-roots with water, obtained a very acrid, nearly inodorous distillate, which, when cooled to a low temperature, deposited needles having a silky lustre, neutral, of burning taste, fusible, and perfectly volatile.

Preparation. 1. The roots, ground to a pulp, are exhausted with cold water; the filtrate is evaporated; and the extract exhausted with alcohol, and allowed to evaporate spontaneously (Saladin). — 2. The roots are exhausted with alcohol of 70 p. c.; the tincture is evaporated; and the extract freed from wax by ether, and from mucous bitter substance and salts by cold water. The residue is dissolved in boiling water; the solution filtered and evaporated; and the extract is dissolved in absolute alcohol. The alcoholic solution is again evaporated, and the cyclamin left behind is decolorised by solution in alcohol and treatment with animal charcoal (Buchner & Herberger). — 3. The washed and comminuted roots are digested in an equal weight of alcohol for 45 days in the dark; the alcohol is decanted; and the residue is pressed, and again twice treated with alcohol. The mixed tinctures are then distilled to remove the alcohol, and the residue is dried in*the water-bath without exposure to light, afterwards re-dissolved in alcohol and allowed to evaporate spontaneously. In about 40 days, white amorphous masses of cyclamin separate, and may be purified by washing with cold, and dissolving in boiling alcohol, from which they are precipitated on cooling (Luca). — 4. The roots of sow-bread, collected in autumn, are sliced, well dried, and reduced to a coarse powder, of which six pounds are placed in a still, together with 15 volumes of alcohol of sp. gr. 0·817 to 0·825, and allowed to stand over night. In the morning, 1½ or 2 volumes of the alcohol are distilled off, and when the remainder in the still has become cool, the distillate is poured back, and the process repeated twice. The whole is then, while still warm, pressed in a linen cloth, and the solid portion treated afresh with 9 volumes of alcohol. The tinctures are mixed together, distilled until the residue is reduced to 6 volumes, and the contents of the still are emptied, while warm, into a glass vessel. After standing from 4 to 10 weeks, the cyclamin is separated, partly in the form of a crust, partly as powder. It is collected, washed with cold alcohol of sp. gr. 0·817 so long as colouring matter is thereby removed, and crystallised from boiling alcohol, with the help of animal charcoal. By concentrating the mother-liquor and wash-waters, a little more may be obtained, the whole amounting to ₁⁄₁₈th of the dried roots (Martius).

Properties. Small, white crystals (Saladin). White, amorphous, friable mass, without smell or lustre, becoming brown on exposure to light, and swelling up in moist air from absorption of water (Luca). Perfectly uncrystallisable (Martius). Taste, very sharp (Luca), and especially harsh and bitter in the throat (Saladin); not bitter, but extremely sharp and harsh (Buchner & Herberger). Action on the organism, emetic and purgative (Saladin). Poisonous to small animals (Luca & Bernard). (See *N. Repert* 6, 326; 8, 452). Neutral. — An aqueous solution rotates the plane of a polarised ray slightly to the left (Luca).

Calculation according to Martius & Klinger		De Luca. *mean.*	Klinger. *mean.*
40 C 240	.... 56·60	.... 54·54	.... 55·40
24 H 24	.... 5·66	.... 9·12	.... 7·99
20 O 160	...... 37·74	.... 36·34	.... 36·61
$C^{40}H^{24}O^{20}$ 424	.... 100·00	.... 100·00	.... 100·00

The great excess of hydrogen in the analyses renders the correctness of the formula very improbable (Kr).

Decompositions. 1. Aqueous cyclamin exposed to *light* in a closed glass tube, gradually throws down a white, amorphous substance, which dissolves again when the liquid is gently warmed. On heating the solution more strongly, unchanged cyclamin is separated (Luca). In an aqueous or alcoholic solution, cyclamin is almost completely decomposed at a temperature near the boiling point of the liquids (Buchner and Herberger). — 2. *Heated* in a small tube, it is carbonised, and gives off acid vapours without subliming (Buchner and Herberger). It is easily changed by heat, and by alkalis and acids (Saladin). — 3. An aqueous solution is not coloured by *iodine*, or by *bromine* or *chlorine*, but is curdled by the two last (Luca). — 4. It dissolves in *hydrochloric acid*, and curdles when warmed, with formation of sugar (Luca). On boiling with dilute acids, it splits up into cyclamiretin and grape-sugar:

$$C^{40}H^{24}O^{20} + 4HO = C^{28}H^{16}O^{12} + C^{12}H^{12}O^{12}. \quad \text{(Martius.)}$$
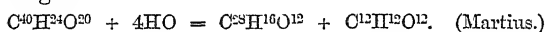
It is not coloured either by hydrochloric or by hydriodic acid (Saladin). 5. *Oil of vitriol* colours cyclamin violet at first (Saladin); yellow, and then permanent violet-red; it is precipitated from the solution by water (Luca). The violet colour does not appear till the liquid is slightly warmed; afterwards carbonisation takes place (Buchner & Herberger.) — 6. *Nitric acid* converts it into oxalic acid (Saladin). — 7. Fused *caustic potash* converts it into a peculiar acid, with evolution of hydrogen (Luca). — 8. Cyclamin does not undergo fermentation with *beer-yeast*, but in contact with *synaptase*, at a temperature of 30—35°, it is decomposed, with formation of fermentable sugar (Luca).

Combinations. Cyclamin is soluble in about 500 parts of *water* (Saladin). Cold water converts it into a transparent, tough mass, and afterwards dissolves it easily. The solution froths like soap-water, becomes turbid at 60—70° from separation of coagulated cyclamin, and clears again after cooling and standing for several days (Luca). The aqueous solution is fluorescent (Martius). — Cyclamin dissolves more readily in aqueous *acids*, even in *vegetable acids*, than in water (Saladin). It is not precipitated from an alcoholic solution by *ammonia* (Buchner & Herberger), or by *metallic salts* (Saladin). Dissolves in aqueous *alkalis* (Luca). According to Martius, it is insoluble in aqueous ammonia, potash, and soda; its aqueous solution forms a white precipitate with the neutral and basic *acetates of lead*, and with *nitrate of silver*, and bluish-white with *sulphate of copper.*
Cyclamin dissolves in *wood-spirit* and in *alcohol.* Soluble in *acetic acid* without separation on heating (Luca). Soluble, according to Luca, insoluble, according to Martius, in *glycerin.* Insoluble in *sulphide of carbon, chloroform* (Luca), in *ether,* and in *oils,* both fixed and volatile. — Completely precipitated by *tincture of galls* (Saladin, Luca).

Carthamin.

$$C^{28}H^{16}O^{14} = C^{28}H^{16}O^{10},O^4.$$
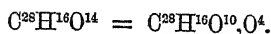
A. Schlieper. *Ann. Pharm.* 58, 357.

Safflower-red. Carthamic acid. — The red colouring matter of the petals

of *Carthamus tinctorius* (*Handb.* viii, *Phytochem.* 68) examined some years ago by Dufour (*Ann. Chim.* 48, 283 ; *A. Gehl.* 3, 481), and Döbereiner (*Schw.* 26, 266). See the erroneous statements of Preisser referred to at page 28, vol. xiv. — Occurs in safflower in quantities of from $\frac{3}{10}$ to $\frac{6}{10}$ per cent. (Salvetat, *N. Ann. Chim. Phys.* 25, 337).

Preparation. Safflower is washed with pure water, or with water containing acetic acid, so long as yellow colouring matter is removed, and then treated with cold alcohol (which dissolves but little of the carthamin) to remove a fatty substance. The residue is beaten to a pulp with water containing 15 p. c. crystallised carbonate of soda, and allowed to stand for some hours, after which it is strained and pressed, and the red alkaline liquid is nearly neutralised with acetic acid. Cotton-wool is then immersed in it, and the carthamin is thrown down thereupon by repeated addition of acetic acid, until the liquid is neutralised. The cotton-wool is taken out after 24 hours, washed with clean water, and immersed for half-an-hour in water containing 5 p. c. crystallised carbonate of soda, whereby the carthamin is extracted. On removing the cotton, and immediately adding to the dark, yellowish-red solution an excess of citric acid, the carthamin separates in flakes, which are washed as much as possible by decantation, and afterwards collected on a filter and dissolved in strong alcohol. By evaporating, first over the water-bath, and afterwards in a vacuum, the carthamin is thrown down in the form of a crust, while a product of decomposition remains in the mother-liquor. The concentrated liquid is mixed with 3 or 4 volumes of water, the precipitated carthamin washed till the wash-water begins to exhibit a pure red colour, and then dried at 100° (Schlieper). A similar method was previously employed by Dufour & Kastner (*Ann. Pharm.* 12, 246.)

Properties. Dark, brown-red powder, with greenish iridescence ; amorphous, even when highly magnified. Dried in a thin layer upon paper, it forms a splendid green film, having a metallic lustre.

	at 100°.			Schlieper. *mean.*
28 C	168	....	56·75	56·9
16 H	16	....	5·40	5·6
14 O	112	....	37·85	37·5
$C^{28}H^{16}O^{14}$	296	....	100·00	100·0

Contains, moreover, 0·3 p.c. nitrogen.

Decompositions. 1. Carthamin yields by *dry distillation,* a small quantity of water and oil, with scarcely any gas, and leaves charcoal, amounting to one-third of its weight (Dufour). — 2. Cloth dyed with safflower bleaches quickly on exposure to light and air (Dufour), and even in the dark at a temperature of 160° (Gay Lussac & Thenard). — 3. Carthamin is decomposed by boiling in *water* or *alcohol,* with formation of a reddish-yellow product, soluble in water, which is not rendered insoluble by repeated solution and evaporation, and is thereby distinguished from safflower-yellow (Schlieper). This product of decomposition remains in solution when, in the above process, the concentrated alcoholic solution is precipitated by water, and may be obtained, by evaporating the solution, as a dark brown, hygroscopic gum. Its solution in water containing acetic

acid, produces, with neutral acetate of lead, a slight precipitate of dark flakes, and, after removing these, ammonia throws down a fine orange-yellow precipitate. This contains, at 100°, on an average 60·12 p. c. oxide of lead, the remainder consisting of 51·24 p. c. C., 4·34 H., and 44·42 O.; represented, therefore, by the formula $C^{28}H^{14}O^{18} + x\,PbO$, and produced from carthamin by absorption of 6 at. O. and loss of 2 at. water (Schlieper). — 4. Carthamin heated with *sulphurous acid*, is dissolved, forming a yellow liquid. — 5. It is not separated from its red solution in *oil of vitriol* by water. — 6. *Nitric acid* precipitates it from an alkaline solution; in contact with the acid the precipitate turns brown, and, on heating, is dissolved with yellow colour. — 7. It is not altered by *hydrosulphate of ammonia*. — 8. A solution of carthamin in dilute *caustic potash* becomes changed, from absorption of oxygen, assuming a bright-yellow colour; the change takes place also in closed vessels, but more slowly. An aqueous ammoniacal solution, which has become yellow by standing, is precipitated by acetic acid in brown flakes, soluble in alkalis, precipitable by acids, and containing 52 95 p. c. C., 5·60 H., and 41·45 O., corresponding to the formula $C^{28}H^{17}O^{16}$. The acetic filtrate gives, with neutral acetate of lead, a second brown precipitate, and at last, on addition of ammonia, yellow flakes containing 69 88 p. c. oxide of lead, the remainder consisting of 49·20 p. c. C., 4·02 H., and 46 78 O.: these are formed from carthamin by absorption of 4 at. oxygen and elimination of 1 at. water ($C^{28}H^{14}O^{20} = 49·12$ p. c. C., 4·09 H., and 46·79 O.). — 9. Carthamin heated with aqueous *bichromate of potash*, is dissolved, forming a yellow liquid. — 10. *Ammoniacal sulphate of copper* throws down, from a solution of carthamin in ammonia, an almost black precipitate, containing cuprous oxide, ammonia, and oxidised carthamin; the filtrate is green.

Carthamin dissolves very slightly in *water*, forming a pale-red solution. It dissolves in *alkalis* and *alkaline carbonates* in all proportions without neutralising them; it is soluble also in aqueous *ammonia*. The deep yellowish-red solutions are precipitated by acids; they undergo decomposition on standing. (See above). Dobereiner described a compound of carthamin and soda, crystallising in colourless, silky needles, which Schlieper was not able to obtain. — Carthamin dissolves in *baryta-water* to a yellow liquid, precipitated by acids; it is not precipitated from solution in ammonia by chloride of barium or calcium. The ammoniacal solution produces, with *protochloride of tin*, a yellowish-brown precipitate, soluble in acetic acid; it precipitates *sesquichloride of iron* brown-red, and *corrosive sublimate* red.

Carthamin dissolves in *alcohol*, with fine purple colour; it is insoluble in *ether* (Schliesser). Insoluble in *volatile* and *fixed oils* (Dufour). It dyes silk, in particular, a fine rose- to cherry-red colour, not permanent.

'   *Appendix to Carthamin.*

Safflower-yellow.

Investigated by Beckmann (*Nov. Comment. soc. reg. Gött. T.* 4, 89) and Dufour. Extracted from safflower by water (p. 203). The acidified aqueous solution is precipitated by neutral acetate of lead; the white precipitate (containing compounds of oxide of lead with vegetable albumen and gum) is removed, and the filtrate neutralised

with ammonia, whereby a dirty orange-yellow precipitate is produced. This is decomposed by dilute sulphuric acid, and the dark-brown solution freed from excess of the acid by means of acetate of baryta. After filtration, the liquid is evaporated in a retort to a syrup, and the safflower-yellow extracted therefrom by absolute alcohol. The alcoholic solution is reduced to a syrup, out of contact with air, and mixed with water, whereby the oxidised safflower-yellow is precipitated, while the unchanged colour remains in solution.

The aqueous solution is of a deep brown-yellow colour, has an acid reaction and a bitter saline taste. It is easily altered by standing or warming in presence of air, and throws down a brown product soluble in alcohol. — A solution of the partially changed safflower-yellow in dilute acetic acid precipitates neutral acetate of lead in dirty-brown flakes, which contain, at 100°, 29·42 p. c. PbO., 38·42 C., 3·21 H., and 28·95 O., corresponding to the formula $C^{24}H^{12}O^{13}$,PbO. The filtrate is precipitated by ammonia in dark-yellow flakes of a compound of the unchanged yellow with oxide of lead containing 63·58 p. c. PbO., 17·85 C., 1·92 H., and 16·85 O., and represented by the formula $C^{16}H^{10}O^{10}$,3PbO. Hence it appears that in the decomposition oxygen is absorbed and water eliminated (Schlieper, *Ann. Pharm.* 58, 358).

Oxygen-nucleus $C^{28}H^{14}O^{12}$.

Carminic Acid.

$$C^{28}H^{14}O^{16} = C^{28}H^{14}O^{12},O^4.$$
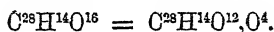
PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 8. 255; *J. Pharm.* 4, 193.
JOHN. *Chem. Schriften* 4, 218.
ARPPE. *Ann. Pharm.* 55, 101.
WARREN DE LA RUE. *Ann. Pharm.* 64, 1; *Phil. Mag. J.* 31, 471; *Mem. Chem. Soc.* 3, 454.
SCHÜTZENBERGER. *Compt. rend.* 46, 47; *J. pr. Chem.* 74, 444; *Chem. Centr.* 1858, 943; in detail *N. Ann. Chim. Phys.* 54, 52.

Carminium. Cochineal-red. Coccusroth. Karminstoff. Principally investigated by Warren de la Rue. Preisser's results (see xv, 28) are given *Rev. scient.* 16, 53; *J. pr. Chem.* 32, 150; Schutzenberger's, below.

Sources. In the various kinds of coccus which yield cochineal. — According to Lassaigne (*Ann. Chim. Phys.* 12, 102), the red of the so-called kermes (*Coccus Ilicis*) is identical with that of cochineal; and, according to Gmelin (*Ed.* 3, 664) probably also the red of stick-lac (*Coccus ficus*) investigated by Funke (*A. Tr.* 18) and by John (*Chem. Schriften,* 5, 15). — According to Bellhomme (*Compt. rend.* 43, 382), the blossom of *Monarda didyma* contains carminic acid.

Preparation. Cochineal is boiled in 40 parts of water for 20 minutes; and the decoction, after being strained and left to itself for three-quarters of an hour, is decanted from the sediment and precipitated by an aqueous solution of neutral acetate of lead, to which a quantity of strong acetic acid equal to ⅓th the weight of the crystals, has been previously added.

The precipitate is washed with boiling water so long as the filtrate precipitates solution of corrosive sublimate, and is afterwards suspended in water and treated with a long-continued stream of hydrosulphuric acid. When the lake is completely decomposed, the filtered liquid is evaporated over the water-bath, and the residue dried, first at a temperature of 38°, and afterwards in a vacuum. The impure carminic acid thus produced contains phosphoric acid and nitrogenous substances, to remove which, $\frac{1}{5}$th to $\frac{1}{4}$th of the acid obtained is precipitated from its aqueous solution by neutral acetate of lead, and the lead-salt is digested with the alcoholic solution of the remainder of the acid, whereby the phosphoric acid is precipitated. The filtrate, mixed with 6 volumes of anhydrous ether, throws down a red precipitate of nitrogenous substances containing a little carminic acid; whilst the pure acid remains in solution, and is' obtained by evaporating the ether-alcoholic solution in a retort, and drying the residue, first in a vacuum, and afterwards at 120°. The carminic acid precipitated by ether, may be recovered by dissolving the precipitate in a little alcohol, and precipitating with a large quantity of ether, whereby the nitrogenous substances are thrown down almost free from the acid (Warren de la Rue).

Cochineal is freed from fat by ether, and afterwards boiled repeatedly with alcohol of 40° B. By evaporating the red tincture, and dissolving the resulting crystals in strong alcohol, the animal substances are separated. The solution, mixed with more than an equal quantity of ether, throws down the colouring matter after standing some time. The liquid from which the crystals were obtained, yields, on evaporation, a residue which is treated in the same manner as the crystals (Pelletier & Caventou). By this process only an impure carminic acid containing nitrogen is obtained, as shown by Pelletier's analyses (De la Rue).

Properties. Purple-brown mass, forming a scarlet-red powder when triturated; not crystalline, or only indistinctly so, but appearing transparent under the microscope. Permanent in the air, and unalterable at 136°. Has a weak acid reaction (De la Rue).

	at 120°.			De la Rue. mean.		
28 C	....	168	....	54·19	....	54·13
14 H	....	14	....	4·52	. .....	4·62
16 O	... .	128	....	41·29	. ..	41·25
$C^{28}H^{14}O^{16}$	....	310	... ...	100·00	.. ..	100·00

Pelletier's carminic acid contained 49·3 p. c. C., 6·7 H., and 3·56 N. (*Ann. Chim. Phys.* 51, 195).

Decompositions. 1. Heated above 136° it yields an acid liquid; and at a red-heat, swells up and gives off a small quantity of red vapour, but no empyreumatic oil. — 2. The aqueous solution does not absorb *oxygen* at ordinary temperatures. — 3. The acid is quickly decomposed by *iodine* and *chlorine*; it forms with *bromine*, on warming or standing, a yellow precipitate soluble in alcohol. — 4. Added to moderately warm *nitric acid* of sp. gr. 1·4, it produces a copious evolution of nitric oxide, and is converted into a mixture of nitro-coccusic and oxalic acids (De la Rue). — Decoction of cochineal is rapidly decolorised by *hydrochloric acid* and *zinc*, more slowly by *hydrosulphate of ammonia* or *hydrated protoxide of iron*, and recovers its colour on exposure to the air (Kuhlmann, *Ann.*

Pharm. 9, 286). Schützenberger's carminic acids exhibit a similar reaction in contact with hydrosulphuric acid (see below).

Combinations. Carminic acid dissolves in *water* in all proportions. — It is soluble without decomposition in strong *hydrochloric acid* and in *oil of vitriol* (De la Rue). The acid of Pelletier & Caventou is carbonised by oil of vitriol.

Carminic acid unites with bases, forming *salts* which, with the exception of the cupric salt, do not exhibit a constant composition. — The aqueous acid is coloured purple-red by the *fixed alkalis* and by *ammonia*, and precipitated purple-red by the *alkaline earths*. In the alcoholic acid, the fixed alkalis and ammonia produce similar precipitates.

Sulphate of alumina throws down from the aqueous acid, after addition of ammonia, a fine carmine-red lake; the acetates of lead, zinc, and silver throw down purple-red precipitates, the last of which is easily decomposed, with separation of metallic silver. With the nitrates of lead, mercury (mercurous salt), and silver, the precipitates are of a reddish colour. Proto- and bi-chloride of tin aqueous carminic acid carmine-red, without precipitation (De la Rue).

The acid of Pelletier & Caventou produces a copious violet precipitate with protochloride of tin. From an aqueous or alcoholic solution, *hydrate of alumina* precipitates a red lake, becoming violet on boiling: if an acid or a salt of alumina be added to the liquid, the hydrate is coloured bright red in the cold, and turns violet when boiled; but if an alkali be added, the hydrate of alumina forms a red lake, which is not rendered violet by long boiling, or even by neutralising the alkali with an acid after boiling. This carminic acid precipitates *nitrate of silver* only when it contains nitrogenous substances.

Carminate of Copper. — An aqueous solution of carminic acid, to which acetic acid has been added, is precipitated by a quantity of acetate of copper not sufficient for complete saturation. — Bronze-coloured, hard mass (De la Rue).

		Dried.			De la Rue. *mean.*
28 C	168	....	48·05	....	47·62
14 H	14	....	4·01	....	4·12
16 O	128	....	36·61	....	36·74
CuO	39·6	....	11·33	....	11·52
$C^{28}H^{14}O^{16}$,CuO.	349·6	... ..	100·00	....	100 00

Carminic acid is soluble in *alcohol* in all proportions. It dissolves only slightly in *ether*, but is not, when pure, precipitated by ether from an alcoholic solution (De la Rue). Insoluble in *oils*, both *fixed* and *volatile*, and is not precipitated by *tannic acid* (Pelletier & Caventou).

Schützenberger's Carminic acids. — According to Schützenberger, cochineal contains two or more coloured acids, one of which may probably be represented by the formula $C^{18}H^8O^{10}$, while the others are, perhaps, $C^{18}H^8O^{12}$, $C^{18}H^8O^{13}$ and $C^{18}H^8O^{14}$. They are obtained, according to his statement, as follows.

1. An aqueous decoction of cochineal is precipitated by chloride of calcium, and the precipitate is decomposed under alcohol with an insufficient quantity of oxalic acid: the red tincture, evaporated to a syrup, throws down, on standing for a day, crystalline tyrosine, which

is removed, and the mother-liquor is diluted, and precipitated by neutral acetate of lead. The precipitate is washed with hot water, and decomposed, either with sulphuric acid in just sufficient quantity, or with hydrosulphuric acid, after which the precipitation and decomposition are repeated two or three times. On evaporating the liquid, a fine red mass is obtained, free from nitrogen and ash, and containing, at 130°, on an average, 52·20 p. c. C., and 4·17 H. When treated with aqueous ammonia, it forms carminamide (see below). — 2. In the preparation of carminic acid, according to 1, the nitrogenous substances may be more quickly removed by fractionating the lead-precipitate ; but the product so obtained has an anomalous composition, and cannot be obtained with constant proportions of carbon and hydrogen, even by repeated precipitation with neutral acetate of lead, and decomposition with hydrosulphuric acid. It contains, at 130°, from 47·94 to 52·19 p. c. C., and from 3·93 to 4·5 H. — A mixture of these acids, dissolved in a small quantity of absolute alcohol, throws down, on addition of ether, a red-brown precipitate (which De la Rue's carminic acid in a pure state does not. Kr.), after the removal of which, the addition of 5 or 6 volumes of ether produces a precipitate of fine red flakes. On evaporating the slightly coloured ether-alcoholic filtrate, it solidifies to a mixture of red needles and crystalline grains, the former of which remain undissolved when treated with boiling ether, while the latter crystallise from the slowly evaporated ethereal solution. The needles contain 49·08 p. c. C., and 4·29 H., corresponding to the formula $C^{18}H^8O^{12} + HO$; the grains, after drying at 130°, whereby a large quantity of water is driven off, contain 55·03 p. c. C., and 4·18 H., the proportions required by the formula $C^{18}H^8O^{10}$, or $C^{22}H^{10}O^{12}$. By evaporating the ethereal solutions, other crystals were obtained, containing 47·32 p. c. C., 3·85 H., and 48·96 C., 3·89 H. — Schützenberger obtained also a soda-salt, crystallising in laminæ; precipitated from a concentrated aqueous solution by alcohol, it contained, at 100°, 35·9 p. c. C., 3·4 H., and 21·2 NaO, corresponding to the formula $C^{18}H^6O^{12}$, 2NaO,3Aq. He obtained further, a carminamide and a carminate of ethyl (see below). — The carminic acids of Schützenberger are decolorised by passing hydrosulphuric acid into their solutions, and recover their colour on exposure to the air.

Carminamide ? — Schützenberger's carminic acid (prepared by method 1) dissolved in water containing ammonia, and set aside for twenty-four hours or longer at a temperature of 30°, becomes altered in its behaviour with protochloride of tin, and leaves, on evaporation over the water-bath, a fine, violet-black, friable residue, which is soluble in water in all proportions, and dissolves also in alcohol, and slightly in ether. It evolves ammonia when boiled with caustic potash, and forms with oil of vitriol a clear brown solution, which, if diluted immediately with water, is precipitated violet, but afterwards brown (Schützenberger). It dissolves in water in all proportions, in alcohol, and sparingly in ether.

		Preliminary calculation.		Schützenberger. mean at 130°.
42 C	....	252	....	52 72	.... 52·81
2 N	... .	28	..	5·85	.. 6·22
22 H	.. ..	22	...	4·60	.... 4·57
22 O	... .	176	....	36 83	... 36·40
$C^{42}N^2H^{22}O^{22}$	....	478	...	100 00	... 100 00

Carminate of Ethyl? — On heating alcoholic carminic acid with hydrochloric acid, two products are formed, resembling each other in some respects, but possessing different degrees of solubility in alcohol. — When a mixture of carminate of soda and iodide of ethyl is heated to 125° for several hours in a sealed tube, iodide of sodium is formed, together with a red substance insoluble in water, which when purified by repeated solution in alcohol and precipitation by water, contains, on an average, 59·03 p. c. C. and 5·29 H.; it dissolves in aqueous alkalis, colours fabrics like cochineal, and appears to be the ethylic ether of carminic acid $C^{18}H^8O^{10}$ (Schutzenberger).

Primary Nucleus $C^{28}H^{28}$.

Methal.

$$C^{28}H^{30}O^2 \;=\; C^{28}H^{28},H^2O^2.$$
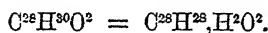
Not known in the pure state. According to experiments cited on page 43, vol. xv, it is to be supposed that methal exists in combination with a fatty acid in spermaceti (Heintz).

Myristic Acid.

$$C^{28}H^{28}O^4 \;=\; C^{28}H^{28},O^4.$$
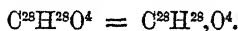
L. Playfair. *Ann. Pharm.* 37, 153; *Phil. Mag. J.* 18, 102.

Heintz. *Pogg.* 87, 267; *J. pr. Chem.* 57, 30; *Pharm. Centr.* 1852, 583; *Chem. Gaz.* 1852, 321; *N. Ann. Chim. Phys.* 37, 361; *Lieb. Kopp's Jahresb.* 1852, 503. — *Pogg.* 90. 137; *Ann. Pharm.* 80. 300; *J. pr. Chem.* 60, 301; *Chem. Gaz.* 1853, 441; *N. J. Pharm.* 25, 71; *Lieb. Kopp's Jahresb.* 1853, 447. — *Pogg.* 92, 429 and 588; *Ann. Pharm.* 92, 291; *J. pr. Chem.* 62, 349 and 482; 63, 162; *Pharm. Centr.* 1854, 585; *Phil. Mag.* [4] 9, 74; *Lieb. Kopp's Jahresb.* 1854, 456. — Summary of the results: *J. pr. Chem.* 66, 1.

Uricochea. *Ann. Pharm.* 91, 369; abstr. *J. pr. Chem.* 64, 47; *Pharm. Centr.* 1854, 942; *Lieb. Kopp's Jahresb.* 1854, 463.

Schlippe. *Ann. Pharm.* 105, 1; abstr. *J. pr. Chem.* 73, 275; *Chem. Centr.* 1858, 279; *N. Ann. Chim. Phys.* 52, 496.

Oudemanns. *J. pr. Chem.* 81, 356 and 367; *Chem. Centr.* 1861, 184 and 192; *Rép. Chim. pure* 2, 390.

Myristicic acid. Myristonic acid. — Discovered by Playfair, and obtained pure by Heintz.

Occurrence. 1. As Myristin. In the nutmeg-butter of *Myristica moschata* (*Handb.* viii. *Phytochem.* 43) (Playfair); in the otoba-fat of *Myristica Otoba*, which seems to contain also oleic, but no third acid (Uricochea). In dika-bread (xv. 44) amounting to more than one-half of the fatty acids contained therein (Oudemanns). — It occurs in

small quantity, together with many other fatty acids (xv. 44), in cocoa-nut oil (Görgey, *Ann. Pharm.* 66, 314 ; Oudemanns) ; in common butter (Heintz) ; in croton oil (Schlippe).—2. In combination with ethal or an analogous body in spermaceti (Heintz). Concerning the occurrence of myristic acid, see further, under *palmitic acid* (C³²H⁶²O⁴), where the fatty acids are mentioned, which were formerly described as independent bodies, but which, according to the investigations of Heintz, must be considered as mixtures.

Formation. By heating ethal with potash-lime (Heintz, Scharling). In so far as the same substance contains methal (p 209) see also xiv, 44.

Preparation. Spermaceti yields only a small quantity of pure myristic acid ; the method given here and xv. 45 serves however, in general, for the separation of the acids obtained from fatty bodies. —*From Spermaceti.* When the fatty acids obtained, together with ethal, by the saponification of spermaceti according to xv. 43, are dissolved in alcohol, in the manner there described, a mixture of palmitic and stearic acids crystallises on cooling, while a portion of both these, and the whole of the myristic and lauric acids (xv. 43) remain in solution. — By fractional precipitation (at last, in presence of excess of ammonia) the alcoholic solution is again divided into two parts—the stearic, palmitic, and a portion of the myristic acid being thrown down as magnesia-salts, the lauric acid and the rest of the myristic acid remaining in solution.

Treatment of the precipitated Magnesia-salts. — The magnesia is separated from the fatty acids by boiling them with dilute hydrochloric acid ; the melting-point of each portion of acid so obtained is determined ; and those portions which melt at nearly the same temperature, and do not differ essentially in their mode of solidifying, are mixed together. When, now, the mixture of acids is repeatedly crystallised from alcohol, and the melting-point of the crystallising portion determined every time, several successive crops of crystals are obtained from each mixture ; and these are to be considered pure : 1. When their melting point remains the same after repeated crystallisations ; 2. When they solidify, on cooling, in crystalline scales ; and 3. When on fractional precipitation of their alcoholic solutions with acetate of magnesia, portions having one and the same melting point are obtained. The several portions of the same acid show also, when pure, the same melting-point after being mixed together as when separate. Sometimes, especially in the preparation of myristic acid, it is necessary to subject the single crystallisations afresh to fractional precipitation, and to repeat the above treatment and examination of the magnesia-salts thus obtained (Heintz).

In this way Heintz obtained, by the first precipitation with acetate of magnesia, nineteen magnesia-salts, from each of which he separated the acids. He mixed together the *first six portions of acid,* the melting-points of which varied from 42·7° to 45°, allowed them to separate from alcohol, and repeated the crystallisation fourteen times ; but even the last crystallisation proved to be a mixture of palmitic and stearic acids, and in no case was a pure acid obtained. By precipitating the mother-liquor from the first nine crystallisations in seven portions with acetate of magnesia, he succeeded in obtaining, from the first, second, and third portions, after eight or nine times repeated crystallisation, pure, or nearly pure, palmitic acid. The fourth and

fifth portions yielded by seven times repeated, the sixth and seventh by three times repeated crystallisation, myristic acid melting at 53·7°, which showed the above signs of purity. Of the remaining acids of the nineteen magnesia-salts, the *seventh* and *eighth portions* did not yield a pure acid by repeated crystallisation, but were recognised as mixtures of palmitic and myristic acids. The 9-17*th portions* were mixed together. The part which first separated from an alcoholic solution did not yield a pure acid on repeated crystallisation; after returning it to the mother-liquor, therefore, a portion of the acids present was precipitated by the addition of a little acetate of baryta. The filtrate mixed with water deposited, in the cold, crystals melting at 53·8°, which, on recrystallisation, yielded pure myristic acid. The acid separated from the *eighteenth* and *nineteenth portions* proved, after three crystallisations, to be also myristic acid (Heintz, *Pogg.* 92, 429).

To prepare myristic acid from *common butter*, Heintz proposes the following method:—The mixture of acids obtained by saponifying butter and decomposing the soap, is freed from volatile acids by boiling with water, and from oleic acid by treating the lead-salt with ether, and afterwards dissolved in alcohol and allowed to crystallise. After removing by recrystallisation as much of the acid present as can be obtained with a melting-point of 56° or 57° (containing palmitic and stearic acids), the collected alcoholic mother-liquors are subjected to fractional precipitation with acetate of magnesia: the myristic acid is then thrown down in ₅the last portions of the precipitate, and may be obtained therefrom by recrystallisation, removing, if necessary, the substances at first precipitable by acetate of baryta (Heintz). — The acids obtained by the saponification of dika-fat yield myristic acid on repeated crystallisation from alcohol, while a second portion of the acid, together with lauric acid, remains in solution. This latter portion may be recovered by precipitating the solution in several parts with acetate of magnesia, separating the magnesia, and crystallising the separate portions of acid until the melting-point rises to 53·8° (Oudemanns).

Playfair saponifies the myristin of nutmeg-butter with strong caustic potash; washes the soap repeatedly with solution of common salt; and afterwards decomposes the hot aqueous solution with hydrochloric acid. The acid, which separates as a colourless oil, solidifying on cooling, when freed from all traces of hydrochloric acid by washing with water, yields, by repeated crystallisation from alcohol, Playfair's myristic acid having a melting-point of 49·8°. (Impure, therefore, and contaminated with an acid containing a smaller proportion of carbon: *Heintz.*) — By saponifying otoba-fat, acids are obtained, from an alcoholic solution of which, acetate of magnesia precipitates only, or chiefly, myristic acid, while oleic acid remains in solution (Uricöchea).

Properties. White, shining crystalline laminæ, resembling palmitic acid; they melt at 53·8°, and solidify on cooling in crystalline scales (Heintz). It has an acid reaction.

Calculation.

28 C	....	168	....	73·68
28 H	....	28	....	12·28
4 O	....	32	....	14·04
C²⁸H²⁸O⁴	....	228	....	100·00

	Playfair.	Heintz.	Uricōchea.	Schlippe.	Oudemanns.
28 C	73·05	.... 73·34	.... 73·10	.... 73·82	.... 73·62
28 H	12·24	.... 12 27	.... 12·34	...... 12·41	.... 12·44
4 O	14·71	..... 14·39	.... 14·56	.... 13·77	.... 13·9 ‡
$C^{28}H^{28}O^4$............	100·00	.... 100 00	.... 100 00	.. .. 100·00	.... 100·00

In the analysis *mean* numbers are given. — Pohl (*Wien. Akad. Ber.* 10, 485) considers $C^{27}H^{-7}O^4$ the correct formula.

Decompositions. Subjected to *dry distillation*, it is partly decomposed and partly volatilised unaltered. No sebacic acid results therefrom (Playfair). On boiling with *nitric acid*, a part is converted into soluble products, with evolution of red vapours, the remaining undissolved portion behaving like unchanged myristic acid (Playfair). By the dry distillation of the lime-salt, myristone is produced (Overbeck). A mixture of myristate and formate of lime yields a repulsive-smelling oil, which deposits a small quantity of a solid product. This last, purified by re-crystallization, forms small, white, crystalline scales, containing a larger proportion of carbon and hydrogen than would be contained in myristic aldehyde (Limpricht, *Ann. Pharm.*, 97, 371). — Myristate of potash heated with *chloro-phosphoric acid*, yields myristic anhydride ; with *chloride of benzoyl*, benzo-myristic anhydride (Chiozza & Malerba).

Combinations. Myristic acid is perfectly insoluble in water. With bases it forms the *myristates* ($C^{28}H^{27}MO^4$). The myristates of the alkalis are not decomposed by water, with formation of acid salts (Playfair).

Myristate of Potash. Myristic acid is digested with concentrated aqueous carbonate of potash, the product evaporated to dryness, and the myristate of potash extracted by absolute alcohol. — White, crystalline soap, easily soluble in water and in alcohol, insoluble in ether (Playfair).

		Playfair.	mean.
28 C.............................	168	.... 63·11	.... 63·20
27 H.............................	27	.... 10·14	.... 10·16
3 O.............................	24	.... 9·02	.... 9·25
KO........................	47·2	.... 17·73	.... 17·39
$C^{28}H^{27}KO^4$	266·2	.... 100 00	.... 100·00

Myristate of Soda. A boiling aqueous solution of carbonate of soda, quite free from sulphate and chloride, is added in excess to boiling alcoholic myristic acid, and the mixture evaporated completely to dryness in the water-bath. The residue is then extracted with boiling absolute alcohol, and filtered boiling hot. The filtrate, which solidifies to a jelly on cooling, is liquefied by warming, and mixed with water in the proportion of one-eighth of the alcohol employed, whereby a mother-liquor is formed, which takes up any foreign salts present. On again solidifying, the salt is collected on linen and strongly pressed (Heintz).

Myristate of Baryta. Obtained from chloride of barium and myristate of potash by double decomposition (Playfair). Heintz precipitates hot alcoholic myristic acid with a hot concentrated aqueous solution of acetate of baryta, and washes the precipitate with weak alcohol and hot water. Oudemanns precipitates an alcoholic solution of the acid

with chloride of barium. — Very light, white, crystalline powder, consisting of microscopic, thin laminæ, having apearly lustre. — Decomposes before melting. Dissolves very slightly in water and in alcohol (Heintz, Playfair).

				Playfair.	Heintz.	Oudemanns.
28 C	168	56·85	56·21	56·92	
27 H	27	9·14	8·94	9·10	
3 O	24	8·12	8·92	8·33	
BaO	76·5	25·89	25·93	25·65	25·34
$C^{28}H^{27}BaO^4$	295·5	100·00	100·00	100·00	

Myristate of Magnesia. Myristic acid, to which ammonia and sal-ammoniac have been added, is precipitated by sulphate of magnesia, and the precipitate washed with water. — Very light powder, consisting of microscopic needles. Becomes transparent at 140°, semi-fluid at 150°, and is decomposed at a higher temperature. The salt dried in the air contains 9·54 p. c. water (3 at.=10·15 p. c. HO) (Heintz).

		At 140°.		Heintz. *mean.*
28 C	168	70 29		69·99
27 H	27	11·30		11·27
3 O	24	10 04		10·38
MgO	20	8·37		8·36
$C^{28}H^{27}MgO^4$	239	100·00		100·00

Myristate of Lead. — The soda-salt, dissolved in weak alcohol, is thrown down by nitrate of lead, and the precipitate washed with alcohol and with water. — White, loose, amorphous powder, which melts to a colourless liquid at 110 — 120°, and solidifies, on cooling, to a white, opaque, amorphous mass (Heintz).

			Heintz.
28 C	168	50·82	50·65
27 H	27	8·16	8·16
4 O	32	9·68	9·95
Pb	104	31 34	31·24
$C^{28}H^{27}PbO^4$	331	100·00	100 00

Aceto-myristate of Lead. On heating myristin with basic acetate of lead for several days, a heavy, white powder, insoluble in water, is produced, containing myristic and acetic acids. — Contains 40·91 p. c. C., 6·65 H., 6·86 O., and 45·58 PbO., corresponding to the formula $4C^{28}H^{27}PbO^4 + C^4H^3,PbO^4$ (Playfair).

Myristate of Copper. — Precipitated from the soda-salt by sulphate of copper. — Bluish-green, very light and loose powder, consisting of microscopic needles. Becomes deeper-coloured when heated above 100°, and cakes together without melting (Heintz).

			Heintz. *mean.*
28 C	168	64·97	64·79
27 H	27	10·44	10·46
3 O	24	9·28	9·37
CuO	40	15·31	15·38
$C^{28}H^{27}CuO^4$	259	100·00	100·00

Myristate of Silver. — Obtained, by double decomposition, from the soda-salt and nitrate of silver. — White, light, amorphous powder, turning slightly grey when exposed to light. — Decomposes above 100°, without melting (Heintz). Dissolves in aqueous ammonia, and forms, by spontaneous evaporation, large transparent crystals (Playfair).

					Playfair. *mean.*		Heintz.
28 C	168	......	50·16	....	48·82	. ...	49·82
27 H	27	....	8·06	,........	7·98	....	8·03
4 O	32	....	9·54	....	10·92	....	9·93
Ag	108	....	32·24	....	32·28	....	32·22
C²⁸H²⁷AgO⁴	335	....	100·00	....	100·00	....	100·00

Myristic acid dissolves easily in hot *alcohol*, crystallising on cooling. It is easily soluble in *ether* (Playfair).

With *Lauric acid* (xiv. 43). — As in general, on melting together two or three fatty acids, a mixture is produced having a melting-point below that of the most difficultly fusible constituent, and in certain proportions below that of either of the acids separately, so when lauric acid is added to myristic acid, the melting point of the latter is lowered. until, when the lauric acid forms 40 p. c. or more of the mixture, the melting-point lies below that of either constituent. Most of the mixtures thus obtained differ in their mode of solidifying from the pure acids (Heintz).

TABLE *of the Melting-points of Mixtures of Lauric and Myristic Acids, according to Heintz :—*

A mixture of—		Melts at	Solidifies at	Mode of Solidifying.
Myristic acid.	Lauric acid.			
90	10	51·8°	47·3°	Crystalline scales.
80	20	49·6°	44·5°	Very fine crystals, not distinguishable as either needles or scales?
70	30	46·7°	39°	Ditto ditto
60	40	43°	39°	Uncrystallised, with isolated lustrous spots.
50	50	37·4°	35·7°	Large crystalline laminæ.
40	60	36·7°	33·5°	Uncrystallised, with isolated lustrous spots.
30	70	35·1°	32·3°	Uncrystallised, wavy
20	80	38·5°	33°	Ditto ditto
10	90	41·3°	36°	Crystalline needles.

Conjugated Compounds of Myristic Acid.

Myristate of Ethyl.

$$C^{32}H^{32}O^4 = C^{28}H^{27}O^3,C^4H^5O.$$
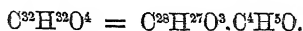
PLAYFAIR. *Ann. Pharm.* 37, 157.
HEINTZ. *Pogg.* 92, 447.

Myristic Ether. — Dry hydrochloric acid gas is passed into a hot solution of myristic acid in absolute alcohol, and the oil which separates on cooling, is washed repeatedly with cold, and afterwards dissolved in a small quantity of warm alcohol. The layer of oil again formed on cooling, after being separated from the alcohol and cooled, deposits large, hard, very easily fusible crystals, from which the mother-liquor is decanted (Heintz). — The sp. gr. of liquid myristic ether is 0·864 (Playfair). — Dissolves easily in hot alcohol and in ether.

				Playfair.	Heintz. mean.
32 C	192	75·0		73·31	74·82
32 H	32	12·5		12·41	12·51
4 O	32	12·5		14·28	12·67
$C^{28}H^{27}O^3,C^4H^5O$	256	100·0		100·00	100·00

Playfair gave the formula $2C^{28}H^{27}O^3,C^4H^5O,HO$.

Myristin.

$$C^{90}H^{86}O^{12} = C^6H^5O^3,3C^{28}H^{27}O^3.$$
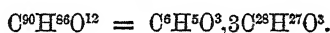
PLAYFAIR. *Ann. Pharm.* 37, 155 ; *Phil. Mag. J.* 18, 102.

Myristearin. Sericin. To be distinguished from Myristicin (xiv. 389). — Occurs in nutmeg-butter, and doubtless also in the fats mentioned on page 210, from which myristic acid has been obtained, with the exception of spermaceti.

Nutmeg-butter was examined by Bollaert (*Quart. J. of Sc.* 18, 317), and Bley. Pelouze & Boudet (*Ann. Pharm.* 29, 41) considered the principal constituent of that substance to be margarin. The fat of the fruit of *Myristica sebifera* and that of *Myristica officinalis* possess characters similar to those of nutmeg-butter. See Bonastre (*J. Pharm.* 19, 186 ; *Ann. Pharm.* 7, 49) ; Brandes (*Ann. Pharm.* 7, 52).

Preparation. The portion of nutmeg-butter insoluble in cold alcohol is dissolved in boiling ether ; the solution filtered hot; and the fat which separates on cooling is pressed between blotting paper, and purified by recrystallisation from ether till the melting-point becomes constant (Playfair). — Powdered nutmegs are exhausted with commercial benzol, and the extract is filtered and allowed to evaporate spontaneously. The crystalline mass thus produced is purified by recrystallisation from a mixture of 2 pts. absolute alcohol and 3 pts. benzol.

By this process 10 p. c. of myristin is obtained from nutmegs (Comar, *N. J. Pharm.* 35, 471; *Kopp's Jahresb.* 1859, 336).

Properties. White, silky, crystalline mass. Melts at 31° (Playfair); that prepared from otoba-fat melts at 46° (Uricöchea, *Ann. Pharm.* 91, 369).

		Calculation according to Weltzien.		Playfair. *mean.*
90 C	....	540	.... 74·82	.... 74·51
86 H	....	86	.... 11·91	.... 12·27
12 O	....	96	.... 13·27	.... 13·22
C⁹⁰H⁸⁶O¹²	....	722	.... 100 00	...... 100 00

Playfair gives the formula C¹¹⁸H¹¹³O¹⁵ (= 4C⁻⁸H²⁸O⁴ + C⁶H⁸O⁶ − 7HO); but Weltzien's formula (= 3C²⁸H²⁸O⁴ + C⁶H⁶O⁶ − 6HO) agrees better with the combining proportions of glycerin, and is in accordance with the results of Playfair's analysis.

Decompositions. Myristin yields, by dry distillation, acrolein and a fatty acid. By long boiling with *basic acetate of lead*, it is resolved into glycerin and myristic acid.

Insoluble in *water*. Soluble in all proportions in hot *ether;* less freely in hot *alcohol.*

Benzo-myristic Anhydride.

$$C^{42}H^{32}O^6 = C^{14}H^5O^3,C^{28}H^{27}O^3.$$
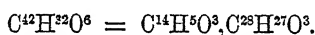
Chiozza & Malerba. *Ann. Pharm.* 91, 104; *J. pr. Chem.* 64, 33; *Pharm. Centr.* 1854, 794.

Myristate of Benzoyl.

Myristate of potash is heated in an oil-bath with an equivalent quantity of chloride of benzoyl, till the smell of the latter is no longer perceptible, and the resulting mass is extracted with boiling ether. The compound crystallises on cooling and evaporation.

Shining laminæ, transparent before drying, melting at 38° to a colourless liquid, and solidifying again at 36°.

Myristone.

$$C^{54}H^{54}O^2 = C^{28}H^{27}O,C^{26}H^{27}O.$$
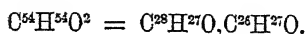
Overbeck. *Pogg.* 86, 587; *Ann. Pharm.* 84, 289.

Obtained from myristate of lime by dry distillation, in the same manner as lauro-stearone (xv, 51) is obtained from laurate of lime.

White, pearly scales, which melt at 75°, and form radiated crystals on cooling. Becomes strongly electric when rubbed. Inodorous, Tasteless.

					Overbeck.
					mean.
54 C	324	....	82·23	....	81·81
54 H	54	....	13 71	....	14 01
2 O	16	....	4·06	....	4·18
$C^{54}H^{54}O^2$	394	....	100·00	......	100·00

Overbeck gives the formula $C^{50}H^{50}O^2$, but the above formula follows from that of myristic acid (*Lieb. Kopp's Jahresb.* 1852, 502).

Myristin does not combine with bisulphite of ammonia or with the bisulphites of the alkalis (Limpricht, *Ann. Pharm.* 94, 246).

Myristic Anhydride.

$$C^{56}H^{54}O^6 = C^{28}H^{27}O^3, C^{28}H^{27}O^3.$$
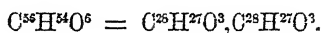
CHIOZZA & MALERBA. *Gerhardt. Traité,* 2, 789.

Obtained from myristate of potash and chlorophosphoric acid by a process similar to that described at page 94, vol. xii.

Indistinctly crystalline fat. The melting-point is several degrees lower than that of myristic acid. — Evolves, on heating, very agreeably smelling vapours. — Difficultly saponified by boiling solution of caustic potash.

Oxygen-nucleus $C^{28}H^{20}O^8$.

Antiarin.

$$C^{28}H^{20}O^{10} = C^{28}H^{20}O^8, O^2?$$
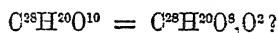
PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 26, 57.
G. J. MULDER, *Pogg.* 44, 414; *J. pr. Chem.* 15, 422; *Ann. Pharm.* 28, 305.

Occurs in the sap of the Upas tree, *Antiaris toxicaria* (*Handbuch* viii., *Phytochem.* 76), which forms a constituent of the arrow-poison of Java.

When the sap (which has been mixed with alcohol to preserve it) is freed from alcohol by distillation, and afterwards exhausted with boiling alcohol, a mixture of vegetable albumin, gum, and wax remains undissolved, while a solution is formed, which throws down, on cooling, wax, antiar-resin, and albumin. On removing the sediment and evaporating, more resin and wax are deposited, and the solution dries up at last to an extract, from a solution of which in boiling water antiarin, amounting to 3·5 p. c. of the dried sap, crystallises. The crystals are purified by washing and recrystallisation (Mulder).

Properties. The crystals (see below) lose their water, when heated, without undergoing further change. — Melts at 220·6° to a transparent liquid, which forms a vitreous mass on cooling. — Heavier than

water. Inodorous. Neutral. Causes death when introduced into the circulation, even in minute portions (Mulder, Pelletier & Caventou).

		Dried.				Mulder. *mean.*
28 C	....	168	....	62·69	....	62·38
20 H	....	20	....	7·46	....	7·44
10 O	....	80	....	29·85	....	30·18
C²⁸H³⁰O¹⁰	....	268	....	100·00	....	100·00

Heated to 249·5°, it turns brown and gives off acid vapours without subliming. — Cold *oil of vitriol* turns it brown, and decomposes it (Mulder).

Combinations. With 4 at. Water. Splendid silvery laminæ, resembling malate of lime. When heated to 112°, it loses, on an average, 11·86 p. c. water (4 at. = 11·84 p.c. HO) (Mulder).

The hydrated crystals dissolve in 254 parts of water at 22·5°, and in 27·4 parts boiling water (Mulder). Antiarin dissolves more readily in dilute *acids* and *alkalis* than in water, and is not precipitated from its solutions by ammonia or magnesia. — It dissolves in concentrated *hydrochloric* and *nitric acids*, without coloration. Absorbs dry gaseous ammonia and a little hydrochloric acid gas at mean temperatures, but loses both at 100° in a current of air (Mulder).

Dissolves in 70 parts *alcohol*, and in 2,792 parts *ether*, at 22·5° (Mulder). Is not precipitated (contrary to the statement of Pelletier & Caventou) by *tincture of galls* (Mulder).

Appendix to Antiarin.

Antiar-resin. — In the sap of the Upas tree. — Obtained by extracting the dried sap with boiling alcohol, boiling the flakes which separate on cooling, with water, and again dissolving in boiling alcohol; it is precipitated in white flakes on cooling. — Inodorous, white, of glassy fracture, and triturable to a fine powder. Becomes pasty when pressed between the fingers, and melts at 60° to a transparent, colourless elastic mass, which does not become coloured at a temperature of 225°. — Sp. gr. at 20° = 1·032. Has no acid reaction. Not poisonous. Contains, after drying over oil of vitriol, on an average, 81·86 p. c. C., 10·25 H., and 7·89 O., corresponding to the formula C³²H²⁴O² (Calc. 82·75 C., 10·34 H., and 6·91 O.) — Dissolves with yellow colour in cold, and carbonises in hot *oil of vitriol*. Insoluble in *water*. Does not combine with *hydrochloric acid gas* or *ammonia*. Forms a milky fluid with *potash-ley*. From a solution of the resin in alcohol mixed with alcoholic *neutral acetate of lead*, water precipitates flakes containing 23·44 p. c. oxide of lead. Dissolves in 24 parts cold, 44 parts boiling *alcohol*, and in 1·5 parts *ether* (Mulder, *Pogg.* 44, 419).

Primary Nucleus $C^{28}H^{30}$; *Oxygen-nucleus* $C^{28}H^{26}O^4$.

Convallaretin.

$$C^{28}H^{26}O^6 = C^{28}H^{26}O^4,O^2.$$
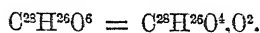
WALZ. *N. Jahrb. Pharm.* 10, 149.

Produced, together with sugar, on boiling convallarin (vid. inf.) with acids. Convallarin is suspended in dilute sulphuric acid, and the mixture boiled ; the convallarin, which at first floats on the surface on the liquid, ultimately cakes together and sinks. — The convallaretin thus formed is separated from undecomposed convallarin by means of ether.

Properties. Yellowish-white crystalline mass, without smell, and having a slight resinous taste.

		Air-dried.			Walz. mean.
28	C	168	....	69·42	69·01
26	H	26	....	10 78	10·81
6	O	48	....	19·80	20·18
$C^{28}H^{26}O^6$		242	....	100·00	100·00

Decompositions. 1. Dissolves in *oil of vitriol* with slight brown colour, and is precipitated by water. — 2. *Nitric acid,* of sp. gr. 1·54, dissolves it with violent reaction. — 3. Not altered by *alkalis.*

Dissolves readily in *ether.*

Glucoside of Convallaretin.

Convallarin.

WALZ. *Jahrb. pr. Pharm.* 7, 281 ; further 8, 78. — *N. Jahrb. Pharm.* 5, 1 ; further 10, 145.

Sources. In *Convallaria majalis.* — Walz (*Jahrb. pr. Pharm.* 7, 171), obtained also from *Convallaria multiflora* (*Handbch.* viii., *Phytochem.* 85) crystals, the nature of which has not been established.

Preparation. From the plant collected, together with the root, during or after flowering time, and dried. The coarsely powdered plant is boiled in water, and the decoction treated as in the preparation of convallamarin (p. 220). The residue is extracted with alcohol of sp. gr. 0.84, and the tincture thus obtained is precipitated with basic acetate of lead and filtered. The filtrate is freed from lead by hydrosulphuric acid, the alcohol distilled off, and the residue allowed to crystallise. The crystals of convallarin, mixed with resin and chlorophyll, are then collected, pressed, and washed with ether. Besides convallamarin, the mother-liquor still contains convallarin, which may

be obtained by either of the following methods. — *a.* The mother-liquor is precipitated with water, which throws down a mixture of convallarin and resin; the latter is removed by ether, and the convallarin crystallised from alcohol with help of animal charcoal. The convallamarin remains dissolved in the water. — *b.* The mother-liquor is nearly neutralised with caustic soda, and evaporated to an extract; this is washed with ether, and the undissolved convallamarin extracted by water; the residual convallarin is then purified by crystallization from alcohol, with the aid of animal charcoal. — If the highly-coloured solutions obtained in the processes *a* and *b* be digested with animal charcoal, a still further quantity of convallarin is taken up, whilst convallamarin remains in solution; the convallarin may be obtained by boiling the charcoal in alcohol.

Properties. Rectangular prisms. Its solution in water or alcohol excites a harsh taste in the throat.

		At 100°.				Walz. mean.
34 C	....	204	......	63·16	......	62·95
31 H	....	31	......	9·60	......	10·17
11 O	....	88	......	27·24	......	26·88
C³⁴H³¹O¹¹	....	323	....	100·00	....	100·00

This formula is given by Walz.

Decompositions. 1. Melts at a temperature above 100°, and *burns* when more strongly heated, leaving charcoal. — 2. By prolonged boiling with dilute *acids*, it is converted into convallaretin and sugar.

$$2C^{34}H^{31}O^{11} + 2HO = 2C^{28}H^{26}O^6 + C^{12}H^{12}O^{12}. \text{ (Walz.)}$$
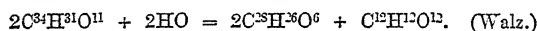
3. Dissolves slowly in *oil of vitriol*, assuming a brown colour. — 4. Dissolves in *nitric acid* of sp. gr. 1·54, with violent frothing and yellow coloration. — 5. Slowly dissolved by cold, and decomposed by hot *caustic potash* solution.

Combinations. Convallarin dissolves very slightly in *water*, but imparts to it the property of frothing like soap-water.

Dissolves easily in *alcohol*, and is precipitated by water or *ether*.

Appendix to Convallaretin and Convallarin.

Convallamarin.

WALZ. *N. Jahrb. Pharm.* 5, 1; further 10, 145.

The bitter principle of *Convallaria majalis.*

Preparation. A decoction of the dried roots, or the decoction of the whole plant obtained in the preparation of convallarin, is precipitated by basic acetate of lead, and filtered; and the filtrate is freed from lead by means of a slight excess of carbonate of soda, and precipitated

with tannic acid. The thoroughly washed and dried precipitate is then exhausted with alcohol, and the tincture is digested with caustic lime to remove tannic acid, and filtered. The filtrate, after distilling off the alcohol, is freed from lime remaining dissolved in it by means of carbonic acid, and afterwards evaporated to dryness. The convallamarin thus obtained still contains resin and ash, the first of which is extracted by ether; to remove the ash the convallamarin is again thrown down from an aqueous solution by tannic acid, and recovered from the precipitate as above.

The aqueous solution obtained in the preparation of convallarin, as described at page 220, yields convallamarin by precipitation with tannic acid, as in the above process.

Properties. White powder, with small crystals intermixed. Has a peculiar, persistent, bitter-sweet taste.

		At 100°.			Walz. mean.
46	C	276	....	53·91	53·71
44	H	44	....	8 59	8·36
24	O	192	....	37·50	37·93
$C^{46}H^{44}O^{24}$		512	....	100 00	100 00

Decompositions. 1. Softens when warmed, and burns without residue at a stronger heat. — 2. By boiling with dilute *acids*, it is converted into convallamaretin and sugar:

$$C^{46}H^{44}O^{24} = C^{17}H^{36}O^{16} + \tfrac{1}{2}C^{12}H^{12}O^{12} + 2HO \text{ (Walz)}.$$
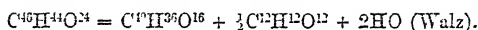
It forms sugar also with *caustic potash.* — 3. *Oil of vitriol* colours the solid substance brown; the aqueous solution a fine violet, decolorised on addition of more water. — 4. Dissolves slowly, with slight yellow colour, in *nitric acid* of sp. gr. 1·54.

Combinations. Convallamarin dissolves readily in *water;* in aqueous *ammonia* it dissolves without colour, and is left unchanged on evaporation. The aqueous solution does not affect most re-agents, but produces a white precipitate, becoming afterwards grey, with *mercurous nitrate,* and a slight turbidity with *chlorine-* and *iodine-water* aqueous *bichloride of platinum,* and *protosulphate of iron.*

Readily soluble in *alcohol,* insoluble in *ether.* — Aqueous convallamarin produces with solution of *tannic acid,* a white precipitate which soon becomes resinous.

Convallamaretin.

Walz. *N. Jahrb. Pharm.* 10, 147.

Produced, together with sugar, by heating convallamarin with acids.

Convallamarin is boiled with dilute sulphuric acid; the resin thereby separated, after washing with water, is dissolved in alcohol; and the solution is treated with animal charcoal, filtered, and left to evaporate. The yellowish-white, indistinctly crystalline mass remaining

behind is treated with absolute ether, whereby a small quantity of admixed substances (derived probably from the convallamarin) is removed.

Yellowish-white, crystalline powder, having a weak, resinous taste.

						Walz.
						mean.
40 C	....	240	....	59·40	....	59·89
36 H	....	36	....	8·91	....	8·99
16 O	....	128	....	31·69	... ...	31·12
C⁴⁰H³⁶O¹⁶	....	404	....	100·00	....	100·00

When heated above 100°, it melts, puffs up and *burns.* — Dissolves slowly in *oil of vitriol,* with reddish-brown colour, and is precipitated by water. — Forms with concentrated *nitric acid,* a yellow solution precipitable by water. — Not altered by *hydrochloric acid, caustic potash,* or *ammonia.*

Dissolves in *alcohol,* and is precipitated from the solution by *water* and *ether.*

Primary Nucleus C²⁸H³⁸; *Oxygen-nucleus* C²⁸H²²O¹⁶.

Kinic Acid.

$$C^{28}H^{22}O^{22} = C^{28}H^{22}O^{16}, O^6.$$
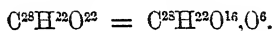
More correctly $C^{14}H^{12}O^{12} = C^{14}H^{12}O^8, O^4.$

HOFFMANN.   *Crell. Ann.* 2, 314.
VAUQUELIN.   *Ann. Chim.* 59, 162.
SCHRADER.   *Berl. Jahrb.* 14, 133.
BERZELIUS.   *Scher. Ann.* 1, 436.
PELLETIER & CAVENTOU.   *Ann. Chim. Phys.* 15, 340; *Schw.* 2, 431.
O. HENRY & PLISSON.   *J. Pharm.* 13, 268; 15, 399; *Ann. Chim. Phys.* 35, 165; *Schw.* 57, 89. — *Ann. Chim. Phys.* 47, 427.
LIEBIG.   *Pogg.* 21, 1. — *Ann. Pharm.* 6, 14; *Pogg.* 29, 70.
BAUP.   *Ann. Chim. Phys.* 51, 57; *Ann. Pharm.* 6, 1; *Pogg.* 29, 64.
WOSKRESSENSKY.   *Ann. Pharm.* 24, 257; *Pharm. Centr.* 1838, 827.
WACKENRODER.   *Repert.* 73, 145.
WÖHLER.   *Ann. Pharm.* 45, 354. — 51, 145; *J. pr. Chem.* 32, 417.
KREMERS.   *Ann. Pharm.* 72, 92; *Pharm. Centr.* 1850, 181.
O. HESSE.   *Ann. Pharm.* 110, 194; abstr. *Chem. Centr.* 1859, 595; *J. pr. Chem.* 77, 376; *Rép. Chim. pure* 1, 419. — *Ann. Pharm.* 110, 333; abstr. *Chem. Centr.* 1859, 631; *J. pr. Chim.* 77, 371; *Rép. Chim. pure* 1, 469. — *Ann. Pharm.* 112, 52; abstr. *Chem. Centr.* 1860, 7; *J. pr. Chem.* 79, 315; *Rép. Chim. pure* 2, 32. — *Ann. Pharm.* 114, 292; abstr. *Chem. Centr.* 1860, 377; *Rép. Chim. pure* 3, 12. Collected Papers, also as Dissertation : *Unters. über die Chinongruppe.* Göttingen, 1860.
CLEMM.   *Ann. Pharm.* 110, 345; *Chem. Centr.* 1859, 681; *J. pr. Chem.* 77, 371; *Rép. Chim. pure* 1, 469.
ZWENGER & SIEBERT.   *Ann. Pharm.* 115, 108; abst. *Chem. Centr.* 1860, 912; *J. pr. Chem.* 82, 246; *Rép. Chim. pure* 3, 73. — *Ann. Pharm.* Suppl. 1, 77.

boiled in water, with addition of quick-lime; the decoction is evaporated, and the kinate of lime thrown down by alcohol. The glutinous precipitate, dissolved in water containing acetic acid, is freed from colouring matter by addition of neutral acetate of lead, then filtered, and the filtrate (freed from lead) is evaporated to a syrup, from which the kinate of lime crystallises after some days (Zwenger).

C. From Coffee-beans. The thoroughly dried (or roasted) and coarsely powdered beans are boiled repeatedly in water; the decoction, after being mixed with milk of lime, is concentrated, first over an open fire, and later, after filtration, on a water-bath, to a syrup ; twice its volume of alcohol is then added, and the precipitate thereby formed is separated, after 24 hours, from the solution, which contains caffeïn. The precipitate is washed with alcohol, pressed, and dissolved in hot water. The filtered solution is slightly acidified with acetic acid and precipitated with neutral acetate of lead, whereby tannate of lead and other substances are thrown down ; and after separating these by filtration, the kinic acid is precipitated with basic acetate of lead. The lead-salt thus obtained, after being washed and decomposed under water with hydrosulphuric acid, yields aqueous kinic acid, which is converted into the lime-salt by neutralisation with carbonate of lime (Zwenger & Siebert).

The kinate of lime is purified by repeated crystallisation, or by precipitating it with alcohol of 36° B. and dissolving in alcohol of 18° B.

Separation of the acid from the lime-salt. 1. A solution of the lime-salt in water is decomposed by an exactly equivalent quantity of oxalic acid, filtered from the oxalate of lime, and evaporated to crystallisation (Vauquelin). Hesse employs a slight excess of oxalic acid, which he removes from the filtrate by means of neutral acetate of lead ; the excess of lead is then removed by hydrosulphuric acid. — 2. An aqueous solution of the salt is precipitated by basic acetate of lead ; the washed precipitate, suspended in water, is then decomposed by hydrosulphuric acid, and the solution is filtered and evaporated (Berzelius). — 3. The lime-salt is decomposed by an aqueous or alcoholic solution of sulphuric acid.

Properties. — Large, hard, transparent, colourless, tabular crystals, belonging to the oblique prismatic system, with characteristic hemimorphism on the right side of the horizontal axis. — (Fig. 83) $u : u = 146°$ 8'; $i : u = 125°$ 75' (Woskresensky). Knop distinguishes the following forms : 1. (Fig. 81), the right edge $u : u$ being perpendicularly truncated by a face t (Fig. 82); $u : u = 132°$ 20' and 47° 40'; $i : u = 127°$ 20' and 52° 40'. — 2. The same, with truncation of the lower front and upper back edges, $u : i$, by 4 octahedral faces O'; $O' : i = 112°$ 12' (obs.) $= 112°$ 5' (calc.); $O' : u = 121°$ 20' (obs.) $= 120°$ 30' (calc.) — 3. The same, but with truncations by O' occurring on the right side side only; between $i : t$ on the right above and below, there are two truncations α (Fig. 85) and β, between α and t; $\alpha : i = 154°$ nearly (obs.) $= 154°$ 25' (calc.) $\alpha : a = 128°$ nearly (obs.) $= 128°$ 50' (calc.); $\beta : i$ 108° 40'. — 4. The same combination, but with the octahedral faces as in 2. — 5. The left u-faces, right t-face, and the two octahedral faces of 3. — 6. Four u-faces, an i-face, m-face (Fig. 84), β-face above and below, and the two octahedral faces of 3. — 7. The left u-faces, right t-face, right β-faces above and below, the two octa-

hedral faces of 3, and an *i*-face. — 8. The left *u*-face and the two octahedral faces *O'* of 3. — 9. The crystals prepared by Zwenger from the bilberry plant exhibit the faces *i* and *u*, on the left the *z*-faces above and below, on the right the two *O'* faces of 3 ; also *t*, *β*, *α*. — The character of the crystals is either prismatic by predominance of *u*, or tabular from predominance of *i*; mostly, however, rhombo-sphenoidal (Ad. Knop, *Ann. Pharm.* 119, 328).

Sp. gr. 1·637 at 8·5° (Henry & Plisson). Does not lose weight at 100°. Melts, with loss of water (see below), at 161·6° (corrected) (Hesse, Zwenger & Siebert), at 155° (Woskressensky); becomes soft and sticky at a little over 100°, and melts at 140° (Clemm). Solidifies, on cooling, to a hard, amorphous mass. Molecular rotatory power to the left; greater in a solution prepared with cold than in one prepared with hot water; least of all in a solution of the fused acid (Hesse).

	Crystals.		Liebig.		Woskres-sensky.		Hesse.
14 C	84	43·75	43·51		43·50		43·8
12 H	12	6·25	6·30		6·28		6·1
12 O	96	50·00	50 19		50·22		50·1
$C^{14}H^{12}O^{12}$	192	100 00	100·00		100·00		100·0

	Clemm.		Zwenger. *a.*		Siebert. *b.*
C	43·38		43·51		43·50
H	6·51		6·55		6·45
O	50·11		49·94		50·05
	100·00		100·00		100·00

The analyses are given in mean numbers : *a* was obtained from coffee-beans, *b* from the bilberry plant (Zwenger & Siebert). — Henry & Plisson (*J. Pharm.* 15, 395) found 10 p. c. carbon less; Baup, who found 47·62 p. c. C. and 5 82 H. may, according to Hesse, have analysed kinide. — Liebig first gave the correct formula (*Ann. Pharm.* 27, 259) ; Gerhardt (*Traité* 3, 132) and others doubled it to $C^{28}H^{24}O^{24}$ + 2 aq., regarding the acid as bibasic, and supposing the presence of water of crystallisation in it and in the silver-salt ; Hesse and Clemm contradicted Gerhardt's view, and confirmed the correctness of Liebig's formula.

Decompositions.—1. Kinic acid *heated* to 220—225° (becoming brown in the latter case, loses water and is converted into kinide :

$$C^{14}H^{12}O^{12} = C^{14}H^{10}O^{10} + 2HO \text{ (Hesse)}.$$
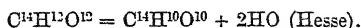
The evolution of water begins at 155°, and amounts to between 4·7 and 5·2 p. c. (Woskressensky). At about 165° the acid evolves 10 p. c. water, without attaining a constant weight; at 220° the loss amounts to more than 13 p. c. (Hesse). Clemm's acid became brown between 160° and 170° and decomposed, giving off bubbles, probably, according to Hesse, because it still contained sulphuric acid. — Kinic acid, which has been heated over 200°, contains small quantities of carbohydrokinonic acid, recognisable by means of sesquichloride of iron (Hesse).

2. Subjected to *dry distillation*, in a retort, kinic acid melts, boils, and at about 280° becomes brown, giving off water and a gas which

burns with pale-blue flame. When more strongly heated it yields a
sublimate of yellowish prisms, which melt and condense to an oily
distillate containing hydrokinone (xi. 161), benzoic and carbolic acids,
benzol, and salicylous acid (Carbohydrokinonic acid ? Kr.) The black-brown
residue swells up strongly at last (Wöhler). Formation of hydrokinone:

$$C^{14}H^{12}O^{12} = C^{12}H^{6}O^{4} + 2CO + 6HO.$$
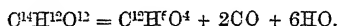
The crystals of the distillate, separated from the oily portion, form Pelletier &
Caventou's *pyrokinic acid*. — The salts of kinic acid yield, by dry distilla-
tion, formic acid and a sublimate of kinone (xi. 158) (Woskressensky).
By the dry distillation of kinic acid, sometimes hydrokinone, sometimes
ericinone ($C^{24}H^{12}O^{9}$), is formed, according as the acid is in combination
with bases or in the free state; in the case of baryta- and lime-salts
pyrocatechin (xi. 379) is also produced (Zwenger & Siebert). — Kinic
acid, when quickly heated, *burns* with yellow flame, emitting the odour
of burning tartaric acid (Wackenroder).

4. A solution of kinic acid in aqueous phosphoric acid evolves large
quantities of gas when concentrated, and on addition of water throws
down a brown substance, whilst phosphohydrokinonic acid remains in
solution (Hesse). Formation of phosphohydrokinonic acid:

$$C^{14}H^{12}O^{12} + PO^{5},3HO = C^{12}H^{7}O^{5},PO^{5} + 2CO + 8HO.$$
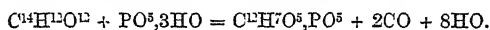
A solution of the lime-salt, obtained by neutralising the acid with carbonate of lime,
breaks up, on standing or warming, into hydrokinone and phosphate of lime; on
adding neutral acetate of lead to the solution, phosphohydrokinate of lead is produced,
part of which separates as a white precipitate, the remainder being thrown down by
ammonia as a pale-yellow precipitate. Both precipitates break up on drying, with
liberation of kinone (Hesse). — 5. Kinic acid dissolves in moderately warm
oil of vitriol, with evolution of carbonic oxide and formation of bisul-
phohydrokinonic acid:

$$C^{14}H^{12}O^{12} + 4SO^{3} = C^{12}H^{6}S^{4}O^{16} + 2CO + 6HO.$$
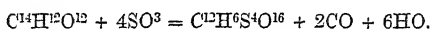
At about 100° sulphurous acid is also given off (Hesse). The solu-
tion, which is colourless at first, becomes grass-green when heated,
and lastly black (Henry & Plisson). Anhydrous sulphuric acid (and
fuming oil of vitriol) also produces bisulphohydrokinonic acid, but car-
bonises a large quantity of the kinic acid (Hesse).

6. *With Chlorine.* On distilling kinic acid or kinate of copper with
oxide of manganese, common salt, and dilute sulphuric acid, an acid
liquid and a yellow crystalline distillate are obtained, the mixture in
the retort swelling up violently at first, and evolving carbonic acid
and a little chlorine. The distillate contains aqueous formic acid,
chlorokinone (xi. 185), bichlorokinone (xi. 188), terchlorokinone (xi.
193), and chloranil, as well as pentachloracetone $C^{6}HCl^{5}O^{2}$ (xiii. 465,
formerly known as *α-oil*). By boiling aqueous kinic acid with hydrochloric
acid and chlorate of potash (the proportions being such that a constant
evolution of chlorine and chlorous acid is maintained) chlorinated
substitution-products of kinone are likewise formed at first; they
distil over together with pentachloracetone, and by pouring back the
distillate and continuing the boiling, may be converted into this latter
substance. Products less rich in chlorine, derived from acetone, may
also be obtained (Städeler, *Ann. Pharm.* 69, 300, and 111, 293). Carbo-
hydrokinonic acid may be detected after the action of chlorate of potash and hydro-

chloric acid on a dilute solution of kinic acid (Hesse). — 7. *Bromine*, dropped into an aqueous solution of kinic acid, forms carbohydrokinonic acid. With pure kinic acid no gas is evolved, but long pale-yellow needles at once make their appearance; they are insoluble in water, and amount to scarcely $\frac{1}{150}$th of the kinic acid employed (Hesse).

8. *Nitric acid* converts kinic into oxalic acid; a peculiar acid being also formed at the beginning of the action (Henry & Plisson). — 9. Kinic acid heated with *oxide of manganese* and dilute *sulphuric acid* yields kinone and carbonic acid (Woskressensky). — 10. *Peroxide of lead*, added to an aqueous solution of kinic acid, evolves carbonic acid and forms hydrokinone (Hesse).

$$C^{14}H^{12}O^{12} + 2PbO^2 = C^{12}H^6O^4 + 2CO^2 + 6HO + 2PbO.$$
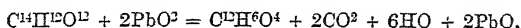
Part of the kinic acid combines with the oxide of lead formed, and is then not decomposed, or is but slowly decomposed by boiling, with simultaneous formation of a basic salt (Hesse). — 11. Kinic acid is not altered by boiling with an aqueous solution of *bichromate of potash* (Wackenroder). — 12. On boiling an aqueous solution of kinic acid with *nitrate of silver* and excess of caustic potash, metallic silver is reduced (Wackenroder). — 13. Heated with *aniline*, it is converted into kinanilide (Hesse). — 14. It is not altered by emulsin (Schoonbroodt, *Pur. Soc. Bull.* 1, 107).

Combinations. Kinic acid dissolves in $2\frac{1}{2}$ parts of water at 9°, and in a much smaller quantity of hot water (Henry & Plisson). The solution becomes mouldy on standing. A concentrated solution forms a thick, syrupy liquid.

Kinic acid expels carbonic acid from its salts. It is *monobasic* (Hesse, Clemm). The general formula of its salts is $C^{14}H^{11}MO^{12}$; neither bi-acid nor double kinates are known (Henry & Plisson, Hesse, Clemm). The preparation of a bibaytic salt, corresponding to neutral salicylate of baryta (xii. 251), has not been effected (Clemm). In the quadroplumbic salt, in the ferric salt, and in the bicupric salt more than 1 at. hydrogen is replaced by metal, in the last at least after drying; Hesse regards it before drying as $C^{14}H^{11}CuO^{12}.CuO,HO + 2$ aq. — The salts of kinic acid are for the most part crystallisable, and have a neutral reaction: with the exception of the basic lead-salt, they are soluble in water, but insoluble in alcohol stronger than 32° B. They are thrown down by strong alcohol in the form of glutinous precipitates. Their water of crystallisation is expelled with difficulty, being generally retained at 100°. Decomposition by heat, see above. — Kinic acid acts like tartaric acid in preventing the precipitation of metallic oxides by caustic potash (Hesse).

Kinate of Ammonia. — A neutral solution of kinic acid in ammonia becomes acid on evaporation, even in a vacuum, from loss of ammonia, and does not leave a crystalline residue (Henry & Plisson). Ammonia, to which an excess of kinic acid has been added, is not precipitated by absolute alcohol, even on long standing (Wackenroder). Crystallised kinic acid evolves carbonic acid from carbonate of ammonia when triturated therewith, and forms a moist coherent mass, which, over the water-bath, gives off the excess of ammonia, and fuses to a neutral mass. This is probably the ammonia-salt (Clemm).

Kinate of Potash. — A bitter gum, not crystallisable, even after

Q 2

addition of free kinic acid (Henry & Plisson). Uncrystallisable syrup (Clemm). The solution behaves towards alcohol like the ammonia-salt (Wackenroder).

Kinate of Soda. — Obtained by neutralising kinic acid with caustic soda, or with the carbonate. Crystallises slowly in fine, transparent, six-sided prisms (Henry & Plisson); in large, pearly white, rhombic prisms or tables (Clemm). Permanent in the air (Henry & Plisson). Not bitter (Baup). Does not lose water of crystallisation at 160° (Henry & Plisson). Melts at 100° to a colourless liquid, with loss of water, but is not rendered anhydrous or decomposed, even at 190° (Clemm). Dissolves in $\frac{1}{2}$ part water at 15° (Baup), less freely in alcohol (Henry & Plisson). — Contains 4 at. water of crystallisation (Baup).

	Crystals.		Clemm. *mean.*
C¹⁴H¹¹O¹¹	183	73·2	
NaO	31	12·4	12·31
4HO	36	14·4	
C¹⁴H¹¹NaO¹²,4aq	250	100·0	

Kinate of Baryta. — Aqueous kinic acid and kinate of potash are not rendered turbid by baryta-water or chloride of barium, but after addition of alcohol, flocks are slowly formed in the liquid (Wackenroder). The neutral salt is obtained by saturating the acid with carbonate of baryta. It crystallises, by spontaneous evaporation of the alcoholic solution, in long, transparent octahedrons, which have a nauseous taste, and effloresce in the air (Henry & Plisson). It is obtained in dihexahedrons with 6 at. water of crystallisation, which do not effloresce in the air (Baup); as a partially crystallised mass (Clemm). The anhydrous salt contains 29·25 p. c. BaO (Henry & Plisson). (Calc. C¹⁴H¹¹O¹¹, BaO = 29·48 p. c. BaO.

	Crystals.		Clemm. *mean.*
C¹⁴H¹¹O¹¹	183	58·37	
BaO	76·5	24·40	24·17
6HO	54	17·23	
C¹⁴H¹¹BaO¹²,6aq	313·5	100·00	

Kinate of Strontia. — a. *With 10 at. Water.* — Easily crystallisable. Resembles the lime-salt, and is perhaps isomorphous therewith, but effloresces speedily in the air, losing 3 at. water, and becomes distinctly pearly. Dissolves in 2 parts water at 12°, and in a smaller quantity of hot water (Baup, Clemm).

	Crystals.		Clemm. *mean.*
C¹⁴H¹¹O¹¹	183	56·34	
SrO	51·8	15·95	16·02
10 HO	90	27·71	
C¹⁴H¹¹SrO¹²,10aq	324·8	100·00	

b. *With 15 at. Water.* — Needles, which effloresce rapidly in the air.

				Clemm. mean.
$C^{11}H^{11}O^{11}$	183	... .	49·49	....	
SrO	51·8	....	14·01	....	13·81
15 HO	135	....	36·50	....	
$C^{14}H^{11}SrO^{12}$,15aq	369·8	... ...	100·00	

Kinate of Lime. — Occurs in cinchona-bark. — Lime-water does not precipitate aqueous kinic acid, even on boiling, and only after long standing when alcohol is added. Chloride of calcium precipitates the aqueous solutions of the alkaline kinates, only after adding alcohol and ammonia, and allowing the mixture to stand (Wackenroder). — Kinate of lime in contact with a solution of lime in sugar-water does not form a basic salt; nor can any other than the mono-acid salt, with 10 at. water, be obtained from a solution to which either alcoholic hydrochloric acid or an excess of kinic acid has been added (Hesse).

With 10 *at Water.* Preparation (p. 224). Rhomboïdal laminæ of 78° and 112°, frequently hexagonal, from having the two acute angles truncated (Baup). Very large transparent tables, which may be bent between the teeth, and are nearly tasteless (Vauquelin, Henry & Plisson). From acid solutions it is obtained in highly lustrous, concentric prisms (Hesse).

When exposed for some days to dry air, it loses from 10 to 12 p. c. water (Liebig). It quickly loses 1 at. water in contact with the air, 7 at. over oil of vitriol (Hesse). The larger crystals, when exposed to the air, acquire a nacreous lustre on the surface without efflorescing (Clemm). — The salt melts in its water of crystallisation when quickly heated to 100°, gives off the water completely at 120°, suffers no further diminution of weight at 180°, and does not turn |brown even at 200°. The dried salt heated to 215°, begins to melt and turns brown, with loss of 1·2 p. c., in consequence of some decomposition (Hesse). — It dissolves in 5 pts. of cold water (Vauquelin); in 6 pts. water at 16° (Baup); much more abundantly in hot water. It is insoluble in highly rectified spirit, but dissolves in spirit of 20 B. (Henry & Plisson). — Its aqueous solution turns the plane of polarisation to the left (Hesse).

					Hesse.		Zwenger & Siebert. a.		b.
		Dried.							
14 C	84	....	39·81	....	39·8	....	39·38	....	39·25
11 H	11	....	5·21	... .	5·4	....	5 15	. ...	5·34
11 O	88	....	41 71	....	41·7	....	41 86	....	42·13
CaO	28	......	13·27	....	13·1	.... ..	13 31	.. ..	13·28
$C^{14}H^{11}CaO^{12}$	211	....	100·00	... ...	100 0	....	100 00	....	100 00

a. From bilbery leaves; *b.* From coffee. — Contains 13·3 p. c. lime (Henry & Plisson); 13·14 p. c. (Liebig).

		Crystals.		Baup.		Liebig.		Hesse.		Clemm.
$C^{14}H^{11}O^{11}$	183	....	60·8							
CaO	28	....	9·3	....	9·38	....	9·18	....	9·33	....	9·17
10HO	90	....	29·9	....	29·56	....	28·81	....	29·77		
$C^{14}H^{11}CaO^{12}$,10aq.	301	....	100·0							

The salt obtained from bilberry leaves contained 29·98 p. c., that from coffee 29·81 p. c. water (Zwenger & Siebert).

Kinate of Magnesia. — White needles, which give off their water of crystallisation at 100°, without melting, either at that temperature or when burnt (Clemm). Permanent in the air; very soluble in water (Henry & Plisson).

					Clemm.
$C^{14}H^{11}O^{11}$	....	183	....	71·21	....
MgO	....	20	....	7·78	..... .	7·80
6HO	. ...	54	....	21·01	.. ....	20·65
$C^{14}H^{11}MgO^{12}$,6aq..	257	....	100·00

Hydrate of alumina does not appear to unite with kinic acid. — The kinates do not precipitate the salts of *chromium* or *uranium* (Vauquelin, Pelletier & Caventou).

Kinate of Manganese. — The alkaline kinates do not precipitate manganese-salts. Pale rose-coloured crystalline crusts, which are unalterable at 180°, and do not melt when burnt. — Soluble in about 200 pts. of cold water (Clemm).

					Clemm.
$C^{14}H^{11}MnO^{11}$	....	183·0	....	83·71	....
MnO	....	35·6	.. ....	16·29	....	16·17
$C^{14}H^{11}MnO^{12}$	....	218·6	....	100·00	....

Kinate of Zinc. — On precipitating the lime-salt with sulphate of zinc, and evaporating the filtrate, dirty white laminæ and small crystalline needles separate out (Henry & Plisson). — White crusts permanent at 180°, and not melting when burnt (Clemm). Very soluble in water (Henry & Plisson).

					Zwenger & Siebert.		Henry &	Clemm.
					a.	b.	Plisson.	
14 C	....	84·0	....	37·56	....	37·25
11 H	....	11·0	....	4·91	....	5·13
11 O	....	88·0	....	39·38	....	39·18
ZnO	....	40·6	....	18·15	....	18·14	.... 18·10	.... 17·79	.... 17·95
$C^{14}H^{11}ZnO^{12}$	....	223·6	....	100·00	....	100·00

a. From bilberry-leaves. *b.* From coffee.

Kinate of Cadmium. — Resembles the zinc-salt in appearance and when heated. Dissolves in about 253 pts. cold water (Clemm).

					Clemm.
$C^{14}H^{11}O^{11}$	....	183	....	74·09	....
CdO	....	64	....	25 91	....	25·97
$C^{14}H^{11}CdO^{12}$	....	247	....	100·00	....

Kinate of Lead. — Neutral acetate of lead does not precipitate kinic acid in aqueous solution, or combined with alkalis, except on addition of ammonia. Basic acetate of lead, added to a concentrated aqueous or alcoholic solution of kinic acid, throws down a copious white precipitate, which is easily soluble in the basic acetate and in water, and becomes crystalline and pearly on standing (Wackenroder).

a. Quadrobasic. Precipitated by basic acetate of lead from kinate of lime (Pelletier & Caventou). An excess of the precipitant dissolves the precipitate: hence it is better not to precipitate completely (Baup). — The boiling solution of the

mono-acid salt is precipitated by ammonia, and the precipitate is quickly washed with boiling water, being protected at the same time from the action of carbonic acid (Woskressensky). It easily absorbs carbonic acid from the air. When heated, it gives off water, without suffering any further alteration at 200°. It dissolves in acetic and other acids.

		at 200°.				Woskressensky.		
14 C	....	84	....	13·91	....	13·53	....	14·93
8 H	....	8	....	1 32	... ...	1·25	....	1·49
8 O	... .	64	....	10·59	....	11·86		
4 PbO	....	448	....	74·18	....	73·36		
$C^{14}H^8Pb^4O^{12}$	....	604	....	100·00	....	100·00		

Contains 72·73 lead-oxide (Baup), 72·52 p. c. (Liebig). — Reichardt (*Chem. Bestandth. der Chinarinden*, Braunschw. 1855), mentions a salt containing 69·34 p.c. PbO at 100°.

b. Mono-basic. — The solution of hydrate of lead in aqueous kinic acid solidifies to an acicular crystalline mass when evaporated on the water-bath (Henry & Plisson). The mother-liquor evaporated to a syrup yields needles, which, after drying in moderately warm air, contain 2 at. water of crystallisation (Baup). Permanent in the air, and has a sweet taste. Dissolves easily in water, also in alcohol of 32° B. (Henry & Plisson).

		At 100°.			Henry & Plisson.
$C^{14}H^{11}O^{11}$	. ...	183	....	62·06	....
PbO	....	112	....	37·94	.... 37·48
$C^{14}H^{11}PbO^{12}$	....	295	....	100·00	....

Acetokinate of Lead. — When aqueous kinic acid is boiled with a large excess of neutral acetate of lead, and the filtrate, evaporated to a syrup, is mixed with alcohol, distinct crystals shoot out, containing acetic as well as kinic acid (Woskressensky).

Ferric Kinate. — Kinic acid protects ferric salts from precipitation by alkalis (Rose). Aqueous kinic acid is not coloured by ferric hydrochlorate (Hesse). The pale yellow solution mixed with ferric hydrochlorate assumes a deeper yellow colour, becoming dark-red on boiling, with formation of ferrous hydrochlorate (Wackenroder). — The red-brown solution of ferric hydrate in aqueous kinic acid, leaves when evaporated a semi-crystalline, very astringent mass, which does not become moist on exposure to the air, but is very soluble in water (Henry & Plisson).

Bi-acid (basic). — Obtained accidentally on quickly evaporating a solution containing kinates and ferric hydrochlorate. Microscopic laminæ having the colour of chromic oxide, soluble in hydrochloric acid. Gives off water over oil of vitriol, then no more at 100°, but decomposes at 170° (Hesse).

		at 100°.			Hesse.
28 C	....	168	....	38·44	.... 38·0
21 H	....	21	....	4·82	.... 4·8
2 Fe	....	56	....	12·82	.... 12·4
24 O	....	192	....	43·92	.... 44·8
$2C^{14}H^{10}O^{10},HO,Fe^2O^3$	....	437	....	100·00	.... 100·0

Kinate of Cobalt. — Separates from the fine dark-red solution, after it has been left for several days to dry up to a syrup, and then diluted with water, in small red nodules, which quickly effloresce and assume a lighter colour. After drying over oil of vitriol, or in the air, it gives off 5 at. water at 150°, and becomes reddish blue. Does not melt when burnt (Clemm).

		Efflorsced.				Clemm.
C¹⁴H¹¹O¹¹	....	183·0	....	68·93		
CoO	....	37·5	....	14·17	....	14·08
5HO	... ...	45·0	....	16·95	....	16·97
C¹⁴H¹¹CoO¹²,5HO	....	265·5	....	100·00		

Kinate of Nickel. — The dark green solution yields, with difficulty, crystalline nodules, which quickly effloresce in the air, and assume a lighter colour. Does not melt when burnt (Clemm).

		Air-dried.				Clemm.
C¹⁴H¹¹O¹¹	....	183·0	....	68·90		
NiO	....	37·6	....	14·16	....	14·24
5HO	... .	45·0	... ..	16·94		
C¹⁴H¹¹NiO¹²,5HO	.. ..	265·6	....	100·00		

Kinates of Copper. — The aqueous solutions of alkaline kinates do not precipitate copper-salts (Vauquelin; Pelletier & Caventou); but on addition of potash-ley, a bluish green precipitate is formed (Wackenroder), which dissolves in excess of alkali (Liebig).

a. Bibasic. — 1. Aqueous kinate of baryta is decomposed by a not quite equivalent quantity of cupric sulphate, and a few drops of baryta-water are added to the clear filtrate, which then, on standing or evaporating, deposits regular crystals (Liebig). — 2. Aqueous kinic acid is boiled with excess of cupric hydrate (Baup), and the filtrate is precipitated with ether-alcohol (Zwenger & Siebert). In this mode of preparation it is difficult to separate the sparingly soluble salt from the excess of cupric hydrate (Liebig). — 3. The salt is likewise formed in small quantity, with evolution of acetic acid, on evaporating a solution of kinate of lime with cupric acetate (Baup, Liebig). Over oil of vitriol it gives off only its adhering water (Kremers), amounting to between 1 and 2·5 p. c. (Hesse). Between 100 and 120°, it gives off 4 at. water of crystallisation (Liebig), and decomposes at a temperature above 140° (Kremers). — Dissolves in 1150 to 1200 pts. water at 18° (Baup).

				Woskres-sensky.	Kremers.	Hesse.	Zwenger & Siebert.
		Crystals.		*mean.*	*mean.*	*mean.*	
14 C	....	84·0	....	29·03	28·17	28·83	28·85	28·84
14 H	....	14·0	....	4.83 ...	4·85	4·95	5·00	5·05
14 O	....	112·0	....	38·71	40·51	38·80	38·90	38·69
2 CuO	....	79·4	....	27·43	26·47	27·42	27·25	27·42
C¹⁴H¹⁰Cu²O¹²,2aq	...	289·4	....	100·00	100·00	100·00	100·00 ...	100·00

Or :

		Crystals.		
C¹⁴H¹⁰O¹⁰	....	174·0	....	60·14
2CuO	....	79·4	....	27·43
4HO	....	36·0	....	12·43
C¹⁴H¹⁰Cu²O¹²,4aq	....	289·4	....	100·00

	Baup.	Liebig.	Kremers.	Hesse.	Zwenger & Siebert.
$C^{14}H^{10}O^{10}$					
2CuO	27·59	.... 47·63			
4HO	14·48	.... 12·83	.... 12·85	.... 12·25	.... 12·43

$C^{14}H^{20}Cu^2O^{12},4aq$ ....

	Dried.			*at 150.*
14 C	84·0	.... 33·15	.... 32·38
10 H	10·0	.... 3·94	.... 3·94
10 O	80·0	..... 31·57	.... 32·56
2 CuO	79·4	.... 31·34	.... 31·12
$C^{14}H^{10}Cu^2O^{12}$	253·4	.... 100·00	.... 100·00

b. Mono-acid. — Obtained by mixing aqueous kinic acid, in excess, with hydrate or carbonate of copper, and cooling the resulting solution, or leaving it to evaporate. Any portion of green basic salt that may be precipitated at the same time, is removed, and the neutral salt is crystallised from water containing kinic acid. — Pale blue laminæ or needles, which contain 5 at. water of crystallisation, and give off $\frac{2}{3}$ of it in contact with the air. The salt dissolves in about 3 pts. of cold water; the solution decomposes on standing, and more quickly when heated, with separation of a basic salt (Baup). Henry & Plisson describe green, easily soluble needles, containing 17·5 p. c. CuO, at 100°, which perhaps belong to this place ($C^{14}H^{11}CuO^{12} = 17·92$ p. c. CuO).

Mercuric Kinate. — Aqueous kinic acid, either free or neutralised with acids, does not precipitate either mercuric or mercurous salts (Vauquelin, Wackenroder). The solution of mercuric oxide in the aqueous acid does not crystallise, but deposits a reddish-yellow powder when heated (Henry & Plisson).

Kinate of Silver. — The alkaline kinates do not precipitate silver-salts (Vauquelin; Pelletier & Caventou) The mixture of aqueous kinic acid, or a kinate, with nitrate of silver, quickly turns black, from separation of metal (Woskressensky). — To prepare the salt, aqueous kinic acid is digested with recently precipitated carbonate of silver, and the liquid, which has become neutral, is evaporated in vacuo without exposure to light (Woskressensky). White, spherical nodules, which quickly blacken when exposed to light (Baup). Does not lose weight at 100° (Hesse). Melts when heated (Clemm). Easily soluble in water, less soluble in alcohol (Henry & Plisson).

	Crystals.		Woskressensky. *mean.*	Hesse.	Clemm.
14 C	84	.... 28·09	.... 28·31	.... 28·2	.... 27·67
11 H.........................	11	.... 3·67	.... 3·75	.... 3·7	.... 3·80
Ag	108	.... 36·12	.... 36·03	.... 35·7	.... 36·13
12 O	96	.... 32·12	.... 31·91	.... 32·4	.... 32·40
$C^{14}H^{11}AgO^{12}$	299	.... 100·00	.... 100·00	.... 100·0	.... 100·00

The silver-salt obtained from bilberry leaves contains 36·10 p. c., that from coffee 36·27 p. c., silver (Zwenger & Siebert).

Alkaline kinates do not precipitate *gold-salts* (Vauquelin; Pelletier & Caventou).

Kinic acid does not unite with *urea* (Hlasiwetz, *Wien. Akad. Ber.* 20. 207). It dissolves in dilute *alcohol* more abundantly than in alcohol of 94 p. c., and is nearly insoluble in *ether* (Wackenroder).

Further Combinations. — With *quinine* and *cinchonine.*

Kinide.

$$C^{14}H^{10}O^{10}.$$
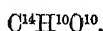
O. HESSE.   *Ann. Pharm.* 110, 335.

Formation. By heating kinic acid (p. 225).

Preparation. Kinic acid is heated in an air-bath to between 220° and 250°; the brown mass is dissolved in boiling alcohol; the brown viscid substance which separates on cooling is removed; and the crystals which separate on spontaneous evaporation are recrystallised from water.

Small crystals resembling sal-ammoniac, which, in presence of certain bases, take up water and are converted into salts of kinic acid — Reaction acid. — Easily soluble in *water* whether cold or hot, sparingly in dilute *alcohol*. No coloration with ferric chloride.

		at 100°·				Hesse. mean.
14 C	....	84	....	48·28	....	48·50
10 H	....	10	....	5·75	. .....	5·95
10 O	....	80	....	45·97	... .	45·55
$C^{14}H^{10}O^{10}$	....	174	....	100·00	.. ....	100·00

Conjugated Compounds of Kinic Acid.

Kinate of Ethyl.

$$C^{18}H^{16}O^{12} = C^{14}H^{11}O^{11},C^4H^5O.$$
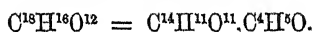
HESSE.   *loc. cit.*

Kinic ether.   Chinasäure Aether.   Chinavinester.

Obtained by heating kinate of silver with iodide of ethyl. The excess of iodide of ethyl is drawn off, and the residue is exhausted with absolute alcohol and evaporated.

Yellow syrup, viscid at mean temperature, mobile at 50°, having a bitter taste and aromatic odour.

		In vacuo.				
18 C	....	108	....	49·09	....	48·8
16 H	....	16	,, ...	7·27	....	7·5
12 O	....	96	....	43·64	....	43·7
$C^{14}H^{11}O^{11},C^4H^5O$	....	220	....	100·00	....	100·0

Appears to distil without decomposition between 240° and 250° in a stream of carbonic acid; but a larger portion of it is decomposed, with intumescence, at a temperature a little above 100°. — When *heated* on platinum-foil, it volatilises at first with a white flame, and finally burns away with a bright flame. — Slowly decomposed by *water*.

Easily soluble in *water* and in *alcohol;* less soluble in *ether.*

Kinanilide.

$$C^{26}NH^{17}O^{10} = C^{14}H^{11}(C^{12}NH^6)O^{10}.$$
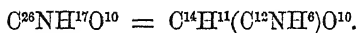
HESSE.   *loc. cit.*

When kinic acid is heated to 180° with excess of aniline, water and aniline are volatilised, and a residue is left which solidifies on cooling. From this substance ether dissolves unaltered aniline, and the remainder, dissolved in ether-alcohol, yields the anilide.

The small, white, silky needles which separate on cooling and evaporation, give off, when heated to 90°, after drying over oil of vitriol, from 6·4 to 6·6 p. c. water (2 at. = 6 32 HO), melt when further heated to 174° (corrected), and solidify in the laminar form. Neutral. Decomposes above 240° without subliming. — Dissolves easily in water and alcohol, sparingly in ether.

		Crystals.			Hesse.
26 C	....	156	....	54·74	.... 54.5
N	....	14	....	4·91	....
19 H	....	19	....	6·66	.... 6·7
12 O	....	96	....	33 69	....
$C^{26}NH^{17}O^{10}$,2HO	....	285	....	100 00	

		At 90°.			Hesse.
26 C	....	156	....	58·42	.... 58·5
N	....	14	....	5·24	....
17 H	....	17	....	6·33	.... 6·5
10 O	....	80	....	30 01	....
$C^{26}NH^{17}O^{10}$	....	267	....	100·00	....

1. Carbohydrokinonic Acid.

$$C^{14}H^6O^8 = C^{12}H^6O^4,2CO^2.$$
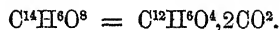
O. HESSE (1859). *Ann. Pharm.* 112, 52; 114, 292; *Untersuchungen über, die Chinongruppe,* Göttingen, 1860. — *Ann. Pharm.* 122, 221.

E. LAUTEMANN. *Ann. Pharm.* 120, 315.

Formation. 1. By the action of bromine on aqueous kinic acid (p. 227). — 2. By heating kinic acid above 200°; by the action of

chlorate of potash and hydrochloric acid on dilute aqueous kinic acid, or of peroxide of manganese and sulphuric acid on aqueous kinate of lime, small quantities of carbohydrokinonic acid are formed, recognisable by ferric hydrochlorate (Hesse).

Preparation. Bromine is added to aqueous kinic acid by portions of 10 drops each, till a portion of it remains undissolved, even after the liquid has been frequently agitated and left to stand for 12 hours. The solution is then decanted from the undissolved bromine, diluted, filtered, and mixed with carbonate of lead, as long as a brisk evolution of gas is thereby set up, and bromide of lead produced. The filtrate, evaporated to a thick syrup on the water-bath, and shaken up with about 5 vol. ether, yields to this liquid carbohydrokinonic acid, which, after the ether has been distilled off, remains as a brown crystalline residue. It is purified by re-crystallisation from water containing hydrochloric acid, with help of animal charcoal. — Or the solution, treated with bromine and filtered, is mixed with carbonate of lead, till this salt begins to take up organic substances; the filtrate is precipitated with solution of neutral acetate of lead, and then, after this precipitate has been collected, a further precipitate is obtained by addition of ammonia. By decomposing the precipitates suspended in water with hydrosulphuric acid, then boiling up and diluting the filtrate, carbohydrokinonic acid is obtained from the first precipitate. The acid obtained from the second lead-precipitate still retains unaltered kinic acid, from which it may be separated by ether (Hesse).

Properties. The crystallised acid is obtained anhydrous by heating to 100° (*vid. inf.*). Melts at 207° (corrected) with partial decomposition, and solidifies in the radio-crystalline form between 160° and 170° (Hesse). When cautiously heated, it sublimes with partial decomposition (Lautemann). — Tastes sour, and at the same time bitter. Reddens litmus (Hesse).

		at 100°.				Hesse. mean.
14 C		84		54·54		54·05
6 H		6		3·90		3·95
8 O		64		41·56		42·00
$C^{14}H^6O^8$		154		100·00		100·00

The following acids give reactions very similar to those of carbohydrokinonic acid. — 1. *Morintannic acid* (xv, 473) and *Morin* (xv, 477), which, according to Hlasiwetz's formula (xv, 474) are isomeric with carbohydrokinonic acid. — 2. *Deuterocatechuic acid* ($C^{16}H^8O^8$) and *Tricatechuic acid* ($C^{18}H^{10}O^8$). These two acids are supposed by Strecker (*Ann. Pharm.* 118, 280) to exist in catechu, inasmuch as he regarded the compound described as pyrocatechin (xi, 379), first as the one one, then as the other of these acids, and, finally, as a mixture of the two. — 3. *Protocatechuic acid.* This acid, according to Lautemann (*Ann. Pharm.* 120, 315), must be regarded as identical with carbohydrokinonic acid, since the latter acid, when heated with pumice, is capable of yielding pyrocatechin (*vid. inf.*). But, according to Hesse (*Ann. Pharm.* 122, 221), the two acids react differently with cupric tartrate, and must, therefore be regarded as only isomeric. — 4. *Oxysalicylic acid.* With regard to this acid, Lautemann (*Ann. Pharm.* 120, 316), thinks it probable that it may be capable of passing into carbohydrokinonic acid (or the latter into oxysalicylic acid). The acids 3 and 4 are here described as an Appendix to Carbohydrokinonic acid.

Decompositions. 1. Carbohydrokinonic acid is resolved by fusion,

and with great facility when heated to 240°, into carbonic acid and hydrokinone (xi, 161):

$$C^{14}H^6O^8 = C^{16}H^6O^4 + 2CO^2 \text{ (Hesse)}.$$
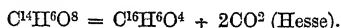
When it is heated with pumice, pyrocatechin is obtained, instead of hydrokinone, the former being apparently capable of passing, under circumstances not exactly known, into hydrokinone (Lautemann, *Ann. Pharm.* 120, 316). — It is not altered by boiling dilute *nitric acid;* the concentrated acid converts it, with rise of temperature and evolution of nitrous acid, into oxalic acid, together with a trace of a yellow substance. — 3. *Anhydrous sulphuric acid* dissolves it, without evolution of gas, forming a blue liquid, brownish by reflected light. No conjugated sulphuric acid can be obtained from this solution.—In *oil of vitriol,* carbohydrokinonic acid dissolves slowly, and chars when heated. — 4. *Bromine* dissolves slowly in the aqueous acid, with evolution of gas. —5. Aqueous carbohydrokinonic acid in contact with *bicarbonate of lime* and air, acquires a dark, nearly black colour, and deposits a black precipitate, which effervesces with acids (Hesse). — 6. From *cupric hydrate* and *potassio-cupric tartrate* aqueous carbohydrokinonic acid separates cuprous oxide ; from *mercuric* and *silver-salts* it separates the metal. Dilute aqueous carbohydrokinonic acid mixed at 8° or 10°, with neutral solution of nitrate of silver, becomes dark-coloured in a quarter of an hour, even in the dark, and in three hours separates metallic silver (Hesse). According to Lautemann (*Ann. Pharm.* 120, 317), aqueous carbohydrokinonic acid reduces nitrate of silver when heated, but not in the cold.

Combinations. With *Water.* — Bihydrated *Carbohydrokinonic acid.* —Furcate groups of needles, also rhombic laminæ or granular crystals. Dimorphous. The granular crystals are distorted twins, belonging to the oblique prismatic system. The terminations of the right prismatic needles could not be observed ; they are rhombic prisms, having the acute edges perpendicularly truncated. Cleavable at right angles to the prismatic faces (Hesse). — Heated to 85°—100°, it gives off, on the average, 10·5 p. c. water (calc. 2 at. = 10·46 HO). (Hesse).

			Dried in the air or over oil of vitriol.		Hesse.
14 C	....	84	....	48·83	.... 48·4
8 H	....	8	....	4·65	.... 4·7
10 O	....	80	....	46·52	.... 46·9
$C^{14}H^6O^8$,2aq.	.... ,.....	172	....	100·00	.... 100·0

Crystallised carbohydrokinonic acid dissolves in 40 or 50 pts. of water at 17°, and very easily in boiling water (Hesse).

With bases the acid forms *salts*, which are, for the most part, easily soluble in water, sparingly soluble or insoluble in alcohol. Hesse regards the acid as monobasic, and the ammonia-salt as a basic salt, in which 1 at. ammonia takes the place of water of crystallisation $C^{14}H^5(NH^4)O^8 + NH^3$. But Strecker's view (*Handwörterb.* 2 [2], 996), which regards the acid as bibasic, is perhaps to be preferred. Carbohydrokinonic acid decomposes the carbonates of the alkaline earths. Its salts turn brown in the air. In contact with a small quantity of sesquichloride of iron, they acquire a violet colour ; with a larger quantity, a fine purple-violet to chrome-green colour, especially in neutral solution (Hesse).

Ammonia-salts. — When dry ammonia-gas is passed over dry carbo-

hydrokinonic acid, 100 pts. of the acid take up from 22·3 to 22·7 pts. of ammonia (2 at. = 22·08 NH³), without giving off water. The resulting compound, freed from excess of ammonia by standing over oil of vitriol, contains 44·7 p. c. C. and 6·2 H., corresponding to the formula $C^{14}H^6O^8,2NH^3$ (calc. 44 68 p. c. C. and 6 38 H.)   When exposed to moist air, it quickly gives off ammonia, and dissolves, with alkaline reaction, in water and alcohol. The latter solution, when evaporated, deposits small acid crystals. Hydrated ether partially dissolves the ammonia-salt, leaving a portion, perhaps consisting of $C^{14}H^6O^8,NH^3 + 2$ aq.   An ether-alcoholic solution of carbohydrokinonic acid becomes turbid when ammonia-gas is passed over it, and then clear, depositing concentric groups of prisms. Brown substances are formed at the same time (Hesse).

The *potash-salt* is precipitated from its aqueous solution by alcohol in the form of a syrup. — The *manganous salt* forms small prisms, easily soluble in water. — The *zinc-salt* forms laminæ. — Aqueous carbohydrokinonic yields a greyish yellow precipitate with *tartaremetic* (Hesse).

Lead-salt. — From aqueous carbohydrokinonic acid, an aqueous or alcoholic solution of neutral acetate of lead throws down an amorphous precipitate, easily soluble in nitric acid, with difficulty in acetic acid.   Part of the carbohydrokinonic acid dissolves at the same time in the acetic acid which is set free, so that the filtrate still gives a precipitate with ammonia (Hesse).

			at 100°—130°.				Hesse. mean.
14 C	......		84·0	......	17·49	......	17·35
5 H	......		5·0	.... ..	1 04	....	1·10
3 Pb	......		311 0	. .....	64 80	.. .	65·40
10 O	. ...		80 0	.... .	16·67	... .	16·15

$C^{14}H^5PbO^8,2PbO$ 480·1 . . 100 00 ...... 100·00

Aqueous carbohydrokinonic acid forms with *ferric hydrochlorate* a dark-green solution, changing to violet on addition of bicarbonate of soda, or of tartaric acid, ferric hydrochlorate, and ammonia (Hesse, Lautemann).

Carbohydrokinonic acid dissolves very easily in *alcohol* and in *ether*. — The aqueous solution does not precipitate a solution of *gelatin* (Hesse).

2. *Protocatechuic acid.* — Obtained, together with oxalic acid, acetic acid, and humous substances, by the action of melted hydrate of potash on piperic acid (xv. 7) :

$$C^{24}H^{10}O^8 + 16HO = C^{14}H^6O^8 + C^4H^4O^4 + C^1H^2O^8 + 2CO^2 + 14H.$$
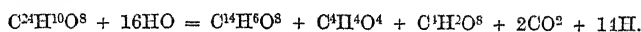
Hydrate of potash is melted in a silver basin with a small quantity of water, piperic acid is added, with constant stirring, and the mixture is heated as long as it continues to give off gas.   The cooled mass dissolved in water, supersaturated with dilute sulphuric acid, filtered, and shaken up with ether, yields to that liquid, protocatechuic acid. — Or sulphuric acid is added to the fused mass in sufficient quantity to produce a slight acid reaction ; the liquid is strongly concentrated, and the residue boiled with alcohol, to remove protocatechuate of potash ; the alcoholic solution is then evaporated, the residue again taken up with water, and the solution precipitated by neutral acetate of lead,

which throws down first yellow, then pure white flocks. The latter, collected, washed with water, and decomposed by hydrosulphuric acid, yield aqueous protocatechuic acid. By evaporation the hydrated acid is obtained in furcate groups of crystals and laminæ. When heated to $100°$, it gives off 2 at. water and leaves $C^{14}H^6O^8$. It has an acid reaction, dissolves sparingly in cold, more easily in hot water; also in alcohol and in ether. It is resolved by heat into carbonic acid and pyrocatechin. Exposed to the air, in contact with excess of bases, it acquires a dark colour. From an ammoniacal solution of chloride of barium, it throws down flocks on addition of alcohol. With solution of neutral acetate of lead, the aqueous acid forms white flocks, $C^{14}H^5O^7,3PbO (=C^{14}H^4Pb^2O^8,PbO,HO)$, which, at $130°$, contain an atom of water less, and dissolve in ammonia, potash, and acetic acid. The latter solution, when evaporated, deposits colourless granules, $C^{12}H^5PbO^8,2HO$, which, at $140°$, give off 2 at. water, and dissolve with difficulty in dilute acetic acid. — Aqueous protocatechuic acid does not colour ferrous salts alone, but if traces of ferric oxide are present, a violet colouring is produced. Mixed with a small quantity of ferric hydrochlorate, it becomes dark green and forms ferrous oxide; the mixture is coloured a deep red by excess of potash, and on subsequent addition of hydrochloric acid, it becomes violet and afterwards colourless. — From potassio-cupric tartrate it does not throw down cuprous oxide, even at the boiling heat: with cupric acetate it at first forms no precipitate, but on standing or warming, it throws down a red powder, soluble with blue colour in tartaric acid. From ammoniacal nitrate of silver it immediately throws down a black precipitate (Strecker, *Ann. Pharm.* 118, 280).

3. *Oxysalicylic acid.* — Obtained by boiling moniodosalicylic acid with potash:

$$C^{14}H^5IO^6 + KO,HO = C^{14}H^6O^8 + KI.$$
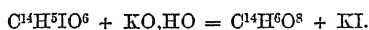
Moniodosalicylic acid (for the preparation of which see *Ann. Pharm.* 120, 300) is dissolved in strong potash-ley, and the solution is boiled down till all the water is expelled, the mass begins to melt, and the whole of the iodosalicylic acid is decomposed. (This is known by the fused mass turning yellow and then brown, as well as by the non-separation of sparingly soluble iodosalicylic acid on treating samples of the liquid with dilute hydrochloric acid). The solution is diluted by pouring it into water, then supersaturated with hydrochloric acid, and left to cool; and the yellow-brown filtrate is treated with ether, to dissolve out the resulting oxysalicylic acid, which remains in coloured crystals on evaporating the ether. It is purified by solution in water, precipitation with neutral acetate of lead, and decomposition of the lead-salt with hydrosulphuric acid. — Highly lustrous, well-developed, concentrically grouped needles, without water of crystallisation, having the composition $C^{14}H^6O^8$, partially fusible without decomposition when cautiously heated, easily soluble in water, alcohol, and ether. — Melts at $193°$ (uncorrected), splits up between $210°$ and $212°$ into carbonic acid and pyrocatechin, mixed with variable quantities of hydrokinone (*vid. sup.*). — With alkalis it instantly assumes a reddish colour, quickly changing to brown; the oxysalicylates of the alkaline earths likewise turn brown and decompose when exposed to the air. — The aqueous acid colours ferric hydrochlorate deep blue, changing to a beautiful violet on

addition of bicarbonate of soda; the latter colouring is also produced on addition of ferric hydrochlorate, tartaric acid, and ammonia. The aqueous acid forms with neutral acetate of lead, a yellowish-white precipitate, easily soluble in acetic acid, insoluble in water; it does not alter nitrate of silver in the cold, but reduces it easily and completely when heated (Lautemann, *Ann. Pharm.* 120, 311).

Ethyl-carbohydrokinonic Acid.

$$C^{18}H^{10}O^8 = C^{14}H^4O^6,C^4H^6O^2.$$
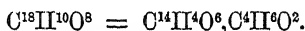
HESSE. (*loc. cit.*)

Carbohydrokinonic ether.

Carbohydrokinonic acid is dissolved in alcohol of 90 p. c.; the solution is saturated with hydrochloric acid gas; the alcohol is distilled off in the water-bath; the residue is shaken up with ether, as long as that liquid takes up a substance which colours ferric chloride; the ether is then distilled off; the brown crystalline residue is shaken up with boiling very dilute alcohol and a small quantity of carbonate of soda; the solution is left to cool; and the acid is again exhausted with ether. The ethereal solution when evaporated leaves coloured crystals, which may be decolorised by again treating them with dilute alcohol, soda, and ether.

Properties. Colourless prisms united in radiate groups, melting at 134° (corrected), and becoming crystalline again at 124·3°. Neutral.

		Over oil of vitriol.				Hesse.
18 C	....	108	....	59·34	....	58 6
10 H	....	10	....	5·19	....	5·5
8 O	....	64	.. ...	35·17	... ..	35·9
$C^{14}H^4O^6,C^4H^6O^2$	....	182	....	100·00	....	100·0

So, according to Strecker. Hesse regards the acid as monobasic, and this compound as the neutral ether.

The ether melts in boiling water before dissolving. — The aqueous solution added to *neutral acetate of lead*, forms a white amorphous precipitate soluble in acetic acid; it colours ferric hydrochlorate violet, changing to purple-violet on addition of a larger quantity of the iron-salt, and finally to chrome-green. It reduces *mercuric chloride, nitrate of silver*, and *potassio-cupric tartrate.*

It dissolves easily in *alcohol*, and especially in *ether*.

Bisulpho-hydrokinonic Acid.

$$C^{12}H^6S^4O^{16} = C^{12}H^6O^4,4SO^3.$$
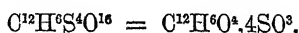
HESSE. *Ann. Pharm.* 110, 195.

Formation, p. 226.

Preparation of the Baryta-salt. Fuming sulphuric acid is poured into fused or finely pulverised kinic acid, till a fresh addition no longer causes any considerable evolution of gas, and the liquid is gently warmed towards the end of the operation, diluted after cooling with a large quantity of water, neutralised with carbonate of baryta, and evaporated to the crystallising point. The crystals which first separate take up a large quantity of colouring matter, so that the mother-liquor yields a less coloured salt.

Free (aqueous) bisulphohydrokinonic acid, obtained by decomposing the baryta-salt with the exactly equivalent quantity of sulphuric acid, or the lead-salt with hydrosulphuric acid, forms an acid syrup.

The acid is *bibasic*, but only the bimetallic salts have been obtained. The salts and the aqueous acid produce with ferric hydrochlorate a fine blue colour, which disappears on heating and reappears with a dingy tint on cooling. The blue colour is also destroyed, slowly by access of air, or by addition of nitric or acetic acid, quickly by addition of hydrochloric, sulphuric, or tartaric acid. A similar action is likewise exerted by sal-ammoniac, chloride of barium, chloride of calcium, sulphate of magnesia, phosphate of soda, neutral acetate of lead, and ferric hydrochlorate. — The salts separate metallic silver from the nitrate.

Ammonia-salt. — Obtained by decomposing the baryta-salt with carbonate of ammonia; separates from the concentrated solution in large crystals.

Potash-salt. — Prepared by neutralising the aqueous acid with carbonate of potash. The bipotassic salt separates even from solutions containing 2 at. acid to 1 at. potash. — Colourless prisms, which have a saline taste, retain 6·9 p. c. water when left over oil of vitriol, give off this water at 150°, and decompose when melted. — Easily soluble in water, sparingly in alcohol.

			Crystals.			
$C^{12}H^4S^4O^{16}$	....	268 0	....	71·79	....	
2K	....	78·4	....	20·99	....	21·3
3HO	....	27·0	....	7·22	....	6 9
$C^{12}H^4K^2S^4O^{16},3HO$	....	373 4	....	100 00	....	

Baryta-salt. Prepared as above described. Beautiful prisms belonging to the oblique prismatic system, with angles of 113° 4′. When heated, it gives off suffocating vapours, hydrokinone, kinhydrone, and water, leaving a residue of charcoal. The salt dried in the air or over oil of vitriol, gives off at 90° from 10·8 to 11·5 p. c. water (6 at. = 11·31 p. c. HO), then between 120 and 160° an additional 3·3 p. c. (2 at. = 3·77 p. c. HO), corresponding in all to 8 at. — The salt dissolves readily in boiling water, with difficulty in cold water, and in alcohol either cold or boiling, but is insoluble in ether.

		Air-dried.				Hesse.
12 C	....	72 0	....	15·08	....	15·50
12 H	....	12·0	....	2·52	....	2·90
2 Ba	....	137·2	....	28·75	....	28·45
4 S	....	64·0	....	13·41	....	13·80
24 O	....	192·0	....	40·24	....	39·35
$C^{12}H^4Ba^2S^4O^{16},8aq$	....	477·2	....	100·00	....	100·00

		at 160°.				Hesse.
12	C	72·0	....	17·76	....	18·4
4	H	4·0	....	0·98	....	1·5
2	Ba	137·2	....	33·86	....	
4	S	64·0	....	15·80	....	
16	O	128·0	.. ..	31·60	....	

$C^{12}H^4Ba^2S^4O^{16}$ .... 405·2 .... 100·00 ....

At 100° it contains 32·45 p. c. (calc. $C^{12}H^4Ba^2S^4O^{16},2aq$ = 32·41 p. c.) (Hesse).

Lime-salt. — Resembles the baryta-salt.

		Crystals.				Hesse.
$C^{12}H^4S^4O^{16}$		268	....	74·03	....	
2	Ca	40	....	11·05	....	11·0
6	HO	54	... ...·	14·92	....	15·0

$C^{12}H^4Ca^2S^4O^{16},6aq$ .... 362 .... 100·00 ....

Lead-salt. — Separated from the concentrated solution of the baryta-salt by neutral acetate of lead, as a bulky precipitate, which quickly changes into yellowish microscopic crystals having a silky lustre. When heated, it assumes a lemon-yellow colour and becomes carbonised. — It is nearly insoluble in water and acetic acid, easily soluble in nitric acid, precipitable by ammonia.

		Over oil of vitriol.				Hesse.
12	C	72·0	....	10·04	....	10·5
6	H	6·0	....	0·84	....	1·1
4	Pb	415 2	....	57·87	....	58·1
4	S	64·0	.....	8·93	....	
20	O	160·0	....	22·32	....	

$C^{12}H^4Pb^2S^4O^{16},2(PbO,HO)$ .... 717·2 ... . 100·00 ....

From aqueous *mercuric chloride*, the baryta-salt crystallises free from mercury.

Bisulphohydrokinonic acid dissolves readily in *alcohol*, but is insoluble in *ether*.

Appendix to Compounds containing 28 at. Carbon.

Thujigenin.

$C^{28}H^{12}O^{14}$.
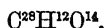
Rochleder & Kawalier.   *Wien. Akad. Ber.* 29, 10.

Occurrence and Formation. Occurs in very small quantity in the *Frondes Thujæ*, the green parts of *Thuja occidentalis*, and is produced, together with sugar, when thujin is heated with hydrochloric acid (p. 246).

Preparation. Comminuted *Frondes Thujæ* are boiled with alcohol; the decoction is strained and left to cool; the deposited wax is separated; the alcohol is distilled from the filtrate; and the residue is

mixed with water, a few drops of solution of neutral acetate of lead being added to facilitate the filtration. The filtrate is completely precipitated by neutral acetate of lead, and the yellow precipitate a, containing thujin and thujetin, is used for the preparation of these substances. The filtered liquid, mixed with basic acetate of lead, yields a second precipitate b containing thujigenin.

a. Preparation of Thujin. The precipitate a is washed with water and dissolved in dilute acetic acid; the liquid is filtered from undissolved matter; the filtrate precipitated with basic acetate of lead; the washed precipitate decomposed under water by hydrosulphuric acid; the liquid heated with the sulphide of lead and filtered hot; the sulphide of lead washed with a small quantity of hot water; and the filtrate, after being freed from hydrosulphuric acid by heating it in a stream of carbonic acid, is evaporated in vacuo over oil of vitriol. The liquid, after standing for some days, deposits crystals of thujin, which are collected, dissolved in boiling water, with addition of alcohol, again left to crystallise, and recrystallised till the solution of the substance in weak spirit no longer turns green on addition of ammonia. — The sulphide of lead still retains a small portion of thujin, which may be obtained by boiling with alcohol.

b. Preparation of Thujigenin. The precipitate b, formed by basic acetate of lead, is washed, suspended in water, and decomposed by hydrosulphuric acid, and the liquid is heated with the sulphide of lead, and filtered hot through a warmed filter. The filtrate, heated as above in a stream of carbonic acid, and evaporated in vacuo, deposits flocks of thujigenin.

c. If the chief object is to obtain thujigenin, the liquids obtained by decomposing with hydrosulphuric acid the two precipitates a and b produced by neutral and basic acetate of lead, are evaporated till thujin and thujetin separate out from them; these substances are removed; and the filtrate is mixed with hydrochloric acid, warmed in the water-bath till it begins to show turbidity, and then quickly cooled. It then deposits thujigenin, which must be collected, dissolved in alcohol, and precipitated by water. — By further heating the liquid from which the thujigenin has separated, and then cooling it, thujetin is obtained, contaminated with a red substance, from which it is purified by repeated solution in alcohol and precipitation by water. — Rochleder supposes that thujenin is formed from thujin.

Properties. Microscopic needles.

	at 100°. *in vacuo.*			Kawalier. *mean.*
28 C	168	.... .	57·53	57·73
12 H	12	....	4·11	3·88
14 O	112	....	38·36	38·39
$C^{28}H^{12}O^{14}$	292	....	100 00	100·00

On substances allied to this, see *Quercetin.*

Decompositions. At *high temperatures*, thujigenin appears to be converted into thujetic acid. So at least Rochleder supposes, because his dried thujigenin gave by analysis rather too much carbon. Thujigenin, in contact

with *chloride of acetyl*, assumes an orange-red colour, and is converted by heat into aceto-thujigenin :

$$C^{28}H^{12}O^{14} + C^4H^3ClO^2 = C^{32}H^{14}O^{16} + HCl.$$
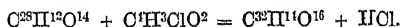
Thujigenin dissolves very sparingly in *water*. — Its alcoholic solution assumes a splendid blue-green colour on addition of *ammonia*.

It dissolves in *alcohol* and is precipitated almost completely by water.

Thujetin.

$$C^{28}H^{34}O^{16}.$$
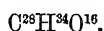
Rochleder & Kawalier.   *Wien. Akad. Ber.* 29, 12.

Formation.   (p. 246).

Preparation.   1. Obtained in the preparation of thujin and thujigenin, as described at page 243. — 2. A warm alcoholic solution of thujin is mixed with dilute sulphuric or hydrochloric acid, and heated till the liquid, which is green at first, and then yellow, has become colourless, and deposits yellow thujetin after evaporation of the alcohol.

		In vacuo at 100°.				Kawalier. *mean.*
28	C	168		54·19		54·20
14	H	14		4 52		4·33
16	O	128		41·29		41·47
$C^{28}H^{14}O^{16}$		310		100·00		100·00

For Hlasiwetz's views on the relations of thujetin to quercetin, see the latter.

By boiling with *baryta-water*, thujetin is converted into thujetic acid :

$$C^{28}H^{14}O^{16} = C^{28}H^{11}O^{13} + 3HO.$$

Thujetin is nearly insoluble in *water*. It is not altered by dilute *hydrochloric* or *sulphuric acid*. Its alcoholic solution assumes a splendid blue-green colour on addition of *ammonia;* green with *potash*, becoming yellow, and finally red-brown on standing, and then yielding red flocks with acids. — It forms red precipitates with the *neutral* and *basic acetates of lead*, colours *ferric hydrochlorate* like ink, and after a while throws down a dark-coloured precipitate. It colours *stannic chloride* dark yellow, *nitrate of silver* blackish grey, and *bichloride of platinum* gradually yellowish brown.

It dissolves in *alcohol* and in *ether*.

Thujetic Acid.

$$C^{28}H^{11}O^{13}.$$
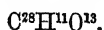
Rochleder & Kawalier.   *Wien. Akad. Ber.* 29, 14.

Formation & Preparation. — 1. Thujetin is boiled with baryta-water. dilute sulphuric acid is added after a while, then alcohol, and the liquid is filtered hot. The filtrate on cooling deposits flocks, which are washed in water, dissolved in alcohol, and reprecipitated by water. — 2. Thujin is boiled for two hours with baryta-water in an atmosphere of hydrogen; carbonic acid is passed into the liquid, till bicarbonate of baryta is formed; the solution then left to cool; and the resulting precipitate is collected, washed with water, and treated with acetic acid, which dissolves the carbonate of baryta, and leaves the thujetic acid   The product may be purified and washed, as in the first process.

Properties.   Lemon-yellow microscopic needles.

	at 100° in vacuo.			Kawalier. mean.
28 C	168	....	59·36	59·37
11 H	11	....	3·88	4·08
13 O	104	....	36 76	36·55
$C^{28}H^{11}O^{13}$	283	....	100·00	100·00

Perhaps isomeric with quercetin (Limpricht *Lehrbuch.* Braunschw., 1862, p. 611). — It probably still retains 1 at. water (Wurtz, *Rép. Chim. pure.* 1, 363).

Thujetic acid dissolves in *alcohol,* and is precipitated by water.

Thujin.

$$C^{40}H^{22}O^{24}.$$
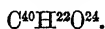
ROCHLEDER & KAWALIER.   *Wien. Akad. Ber.* 29, 10 ; *J. pr. Chem.* 74, 8 ; *Chem. Centr.* 1858, 449 ; *Chem. Gaz.* 1859, 61 and 88.

Occurrence.   In the green parts of *Thuja occidentalis.*

Preparation. (p. 243).   240lb. *Frondes Thujæ* yield a few grammes of thujin.

Properties.   Shining, lemon-yellow crystals, appearing as four-sided tables when viewed by a magnifying power of 380 diameters.
Has an astringent taste.

	In vacuo at 100°.			Kawalier. mean.
40 C	240	....	52·86	52·79
22 H	22	....	4·84	5·04
24 O	192	....	42·30	42·17
$C^{40}H^{22}O^{24}$	454	....	100·00	100·00

On the relations of thujin to quercitrin, see the latter.

Decompositions.   1. Thujin heated on platinum-foil, burns, and leaves a carbonaceous residue, which burns away slowly, but completely. — 2. When heated in alcoholic solution with dilute *hydrochloric* or *sulphuric acid,* it turns green, then yellow, and is resolved into

thujetin, which separates out, and sugar. 100 pts. thujin take up 7·3 pts. water, and yield 40·48 pts. sugar, and 66·78 thujetin.

$$C^{44}H^{22}O^{24} + 4HO = C^{12}H^{12}O^{12} + C^{28}H^{11}O^{16}.$$
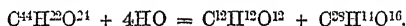
Thujigenin appears also to be formed when thujin is heated for a short time with hydrochloric acid (p. 243). — 3. It dissolves in *baryta-water*, forming a yellow solution, which, when heated, deposits an orange-yellow precipitate of thujetic acid, becoming dark reddish-yellow by continued boiling, while sugar remains in solution :

$$C^{40}H^{22}O^{24} + HO = C^{28}H^{11}O^{13} + C^{12}H^{12}O^{12}.$$
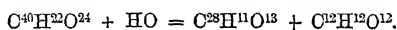
On thujin-sugar, see vol. xv. p. 349.

An alcoholic solution of thujin is coloured yellow by *ammonia* or *potash*, red-brown with access of air, and yields a fine yellow precipitate with *neutral* or *basic acetate of lead*. It is coloured dark-green by *ferric hydrochlorate*, does not precipitate *cupric sulphate*, *bichloride of platinum*, or *nitrate of silver*, but the silver-solution becomes blackish grey on addition of ammonia.

Soluble in *alcohol*.

Acetothujenin.

$$C^{32}H^{14}O^{16} = C^{28}H^{11}O^{13},C^{4}H^{3}O^{3}.$$
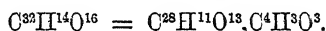
ROCHLEDER & KAWALIER.   *Wien. Akad. Ber.* 29, 18.

Thujigenin is covered with chloride of acetyl in a small flask, and heated for a quarter of an hour, the chloride of acetyl being allowed to flow back, then freed from the excess of chloride of acetyl by distillation. The residue dissolved in alcohol deposits, on addition of water, a coherent resin, which may be dried at 100° in vacuo.

				Kawalier.
32 C	192	57·48	57·15
14 H	14	4·19	4 01
16 O	128	38·33	38·84
$C^{32}H^{14}O^{16}$	334	100·00	100·00

When exposed to the *air* in alcoholic solution, it turns red, and the liquid evaporated over the water-bath, with addition of water, leaves a reddish-yellow residue.

Thuja Oil.

BONASTRE.   *J. Pharm.* 11, 156.
SCHWEIZER.   *J. pr. Chem.* 30, 376; *Ann. Pharm.* 52, 398; *Repert.* 90, 227; *N. J. Pharm.* 5, 268; *Chem. Gaz.* 2, 96.

The oil which passes over on distilling with water the ends of the branches and the leaves of *Thuja occidentalis* (*Handbuch.* viii., *Phytochem.*

79); [amounting to 1 p. c., according to Hübschmann (*N. Br. Arch.* 96, 250)], is colourless (Schweizer); greenish yellow (Bonastre); of sp. gr. 0·925 (Hübschmann); and sharp taste (Schweizer); somewhat peppery (Bonastre). After dehydration, it contains 77·62 p. c. C., 10·92 H., and 11·46 O. When distilled it begins to boil at 190°, the greater part going over between 193° and 197°; the remainder passes over, with yellow colour, between 197° and 206°, leaving only a slight red residue. The oil which distils below 197° contains, on the average, 70·77 p. c. C., 10·68 H., and 18·55 O.; that which passes over between 197° and 206°, contains 76·13 p. c. C., 10·67 H., and 13·20 O.; the crude oil is therefore a mixture of at least two oxygenated oils (Schweizer).

Crude oil of thuja becomes yellow in contact with the *air*. It dissolves large quantities of *iodine*; and on heating the solution, a violent action takes place, hydriodic acid and a very volatile oil being given off. The residue when further heated, gives off a dark viscid oil, then vapour of iodine, and leaves a residue of charcoal (Schweizer).

When the volatile oil just mentioned is repeatedly distilled over iodine, then over quick lime and potassium in succession, it becomes colourless, free from oxygen, like turpentine-oil in taste and odour, lighter than water, and boils between 165° and 175°. Thus purified, it contains Schweizer's *thujone*. — The viscid oil agitated with potash-ley, yields to that liquid, carvacrol (xiv. 414), separable by sulphuric acid. The portion insoluble in potash appears to be colophene (xiv, 279) (Schweizer).

Oil of thuja is not sensibly altered by distillation with *phosphoric acid*. By *oil of vitriol*, it is immediately resinised (Schweizer); turned brown and charred (Bonastre). Commercial *nitric acid* turns it dark yellow, without setting it on fire (Bonastre); with *potassium*, it resinises, without giving off hydrogen (Schweizer). — *Hydrate of potash* blackens thuja-oil immediately, and resinises a portion of it, whilst another portion passes over unaltered. Repeated distillation of the portion which has gone over with hydrate of potash diminishes its quantity, but does not perceptibly alter its external characters; after five distillations the distillate contains 78·87 p. c. C., 10·98 H., and 10·15 O. From the black residue water separates a resin-soap, soluble in pure water, while carvacrol remains in the alkaline solution (Schweizer).

Oil of thuja dissolves sparingly in *water*, in 10 pts. of *acetic acid*, and easily in *alcohol* and *ether*.

COMPOUNDS CONTAINING 30 AT. CARBON.

Primary Nucleus C³⁰H¹⁰.

Succisterene.

C³⁰H¹⁰.

PELLETIER & WALTER. *Compt. rend.* 6, 915; *J. pr. Chem.* 14, 380; in detail, *N. Ann. Chim. Phys.* 9, 96; *J. pr. Chem.* 31, 114.

Occurs among the products of the dry distillation of amber, and is separated from chrysene by the method described in vol. xv., page 2.

White, slender, flat needles, without taste or smell. Melts at 160°, but does not volatilise till heated above 300°, when it distils over like wax, and decomposes to a slight extent, leaving a small quantity of charcoal.

						Pelletier & Walter.
						mean.
30 C	....	180	....	94·73	....	94·28
10 H	....	10	....	5·27	....	5·89
C³⁰H¹⁰	....	190	....	100·00	....	100·17

Succisterene is not altered by cold *mineral acids*, but hot *nitric acid* converts it into a yellow resin. — It dissolves in hot *oil of vitriol* with dark blue colour, without admixture of green, and then quickly chars. The blue solution is decolorised by water, but becomes blue again when concentrated.

Succisterene is insoluble in *alkalis*, nearly insoluble in cold, more soluble in hot *alcohol*; very slightly in *ether*.

It dissolves in *oils*, both *fat* and *volatile*.

Primary Nucleus C³⁰H¹².

Pyrene.

C³⁰H¹².

LAURENT. *Ann. Chim. Phys.* 66, 146.

Preparation. See Chrysene. (xv. 1). The thick oil from which chrysene has crystallised on cooling, is mixed with the ether which has been used to wash the chrysene, then cooled with ice, and decanted from the resulting laminæ, and the mother-liquor is left to evaporate, whereby a few more crystals are obtained. The crystals are freed from adhering oil by spreading them on filtering paper, pressing, distilling till ₁₀/₁₀ has gone over, and washing with a small quantity of ether, and are obtained colourless and free from chrysene, by repeated crystallisation from alcohol.

Microscopic rhombic laminæ, resembling pounded talc when dry, and very much like anthracene (p. 165). Inodorous. Melts between 170° and 180°, solidifies to a lamino-crystalline mass on cooling, and distils without decomposition at a high temperature. Part of the vapour condenses in the form of a pulverulent sublimate.

						Laurent.
30 C	......	180	......	93·75	......	91·91
12 H	......	12	......	6·25	......	6·11
$C^{30}H^{12}$	......	192	......	100·00	......	98·02

Polymeric with naphthalin (xiv. 1).

When thrown on glowing coals, it emits inodorous vapours. — Dissolves in *oil of vitriol* when heated, and then blackens. If chrysene is present, a green colouring is produced. — By warm *nitric acid*, it is easily converted into binitropyrene.

Insoluble in *water*; sparingly soluble in *alcohol* and *ether*; easily in boiling *oil of turpentine*.

Nitro-nucleus $C^{30}X^2H^{10}$.

Binitropyrene.

$$C^{30}N^2H^{10}O^8 = C^{30}X^2H^{10}.$$
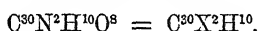
LAURENT. *Ann. Chim. Phys.* 66, 148.

Warm nitric acid decomposes pyrene with facility, and converts it into a thick red-brown oil, which, after removal of the acid, is boiled with water, then with alcohol, and dried.

Very brittle resin, having the colour of gamboge, but redder. Melts in boiling alcohol.

						Laurent.
30 C	......	180	......	63·83	......	64·36
2 N	......	28	......	9·93	......	9·34
10 H	......	10	......	3·54	......	3·66
8 O	......	64	......	22·70	......	22·64
$C^{30}X^2H^{10}$	......	282	......	100·00	......	100·00

Detonates with incandescence on glowing coals or when *heated* in a glass tube. — It dissolves with brown-red colour in *oil of vitriol*. — When treated with hot *nitric acid*, it dissolves, but does not (like anthracene, p. 166) yield needles on cooling. On evaporating the solution and heating the residue, $\frac{1}{100}$ of the binitropyrene sublimes in curved threads, whereas in the case of anthracene, the whole sublimes as oxanthracene (p. 169).

Binitropyrene is insoluble in *water*, and very slightly soluble in *alcohol* and *ether*.

Primary Nucleus $C^{30}\Pi^{20}$; *Oxygen-nucleus* $C^{30}H^{18}O^2$.

Santonin.

$$C^{30}H^{18}O^6 = C^{30}H^{18}O^2,O^4.$$
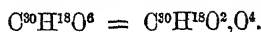
KAHLER. *Br. Arch.* 34, 318; 35, 216.
ALMS. *Br. Arch.* 34, 319; 39, 190.
OBERDÖRFFER. *Br. Arch.* 35, 219.
H. TROMMSDORFF. *Ann. Pharm.* 11, 190.
GUILLEMETTE. *J. Pharm.* 26, 152; *J. Chim. méd.* 16, 168; *Ann. Pharm.* 36, 333.

RODER. *Jahrb. pr. Pharm.* 6, 45.
MIALHE & CALLOUD. *N. J. Pharm.* 4, 387.
CERUTTI. *N. Br. Arch.* 52, 148.
HELDT. *Ann. Pharm.* 63, 10; abstr. *Pharm. Centr.* 1847, 855; *J. pr
    Chem.* 43, 186; *Chem. Gaz.* 1848, 53; *N. J. Pharm.* 13, 65.
CALLOUD. *N. J. Pharm.* 15, 106; abstr. *Ann. Pharm.* 72, 326; *Pharm.
    Centr.* 1849, 413.

Santonic acid. Santoninsäure or *Santonsäure.* Discovered in 1830 by Kahler, and almost at the same time by Alms; investigated chiefly by H. Trommsdorff and Heldt.

Occurrence. In *Semen Cynæ*, the worm-seed of the Levant (*Handbuch* viii, *Phytochem.* 67).

Preparation. 1. Wormseed is heated to boiling with water; milk of lime is added till the red colour at first produced has disappeared; the liquid is strained; and the residue, after being pressed, is again subjected to the same treatment. The liquids clarified by deposition are evaporated, with frequent skimming, to a thin extract, then strained, and mixed, while still warm, with a slight excess of hydrochloric acid, whereupon, after standing for some time, the whole of the resin is deposited, together with a very small quantity of santonin. The liquid filtered therefrom is mixed with a little water, and boiled till crystals of santonin begin to separate on the surface, then left to itself till the crystallisation of the santonin is complete. The resulting crystals are purified by washing with aqueous ammonia, and repeated crystallisation from boiling alcohol with help of animal charcoal (Calloud, Cerutti). Lecocq (*J. Chim. méd.* 1, 529) further boils the crude crystals with milk of lime not in excess, decolorises the solution with animal charcoal, and precipitates with hydrochloric acid. — If the boiling solution of the lime-compound of santonin be supersaturated with hydrochloric acid, and the boiling continued for five minutes longer, the whole of the santonin separates within 24 hours, while the resin remains suspended in the liquid, and may be decanted therewith (Bertram, *N. Repert.* 2, 405; 4, 32).

2. A mixture of 4 pts. wormseed with 2½ pts. dry hydrate of lime is exhausted three times successively with 16 to 20 pts. warm alcohol of sp. gr. 0·94, and the alcohol is distilled from the tinctures till only 12 to 16 pts. remain behind, after which the liquid is filtered, concentrated to one-half, and boiled for a few minutes with excess of acetic acid. On cooling, the greater part of the santonin separates out in large, feathery crystals, and the rest may be obtained by evaporating the liquid to a syrup and diluting with water. The product may be purified by washing with cold alcohol, and recrystallising from boiling alcohol, with help of animal charcoal. The yield is from 1·8 to 1·9 p. c. of the seeds (H. Trommsdorff). — 3. Pulverised wormseed is stirred up to a paste with water and pressed, after being left to itself for 18 hours; this treatment is repeated, and the residue, after drying, is exhausted with alcohol of 89 p. c.; the tinctures are concentrated by distillation and evaporation; and the santonin is left to crystallise out, and purified by pressure, washing with cold alcohol or ether, and recrystallisation (Guillemette, Roder). In this manner a quantity of santonin is obtained, amounting to 1·6 p. c. of the seeds.

On the estimation of santonin, see Schlimpert (*N. Br. Arch.* 100, 119).

Properties. Rectangular four-sided tables belonging to the square prismatic system, with bevelled edges (Rammelsberg). Colourless, with pearly lustre. Easily friable (Alms). Melts between 169° and 170° to a colourless liquid, which solidifies in the crystalline form on cooling (Trommsdorff). Melted santonin, especially that which has been crystallised from acetic acid, solidifies, when quickly cooled, to an amorphous gum, which does not crystallise, even when touched or cut with a hard body. It is restored to the crystalline state by contact with the vapour of alcohol or ether, by moistening it with these liquids, or with acetic, hydrochloric, or nitric acid, or by heating it for some time to between 40° and 50°. Moistening with water, aqueous ammonia, or potash-ley, does not induce the crystallisation (Heldt). It volatilises without decomposition at a few degrees above its melting point, in heavy, white, irritating vapours, which condense to white needles (Trommsdorff). Sp. gr. 1·257 (Alms); 1·247 at 21·2° (Trommsdorff). Inodorous and nearly tasteless; tastes slightly bitter after being kept for some time in the mouth, strongly bitter in alcoholic solution. It exerts an anthelmintic action, but is sometimes fatal to children when given in quickly repeated doses of 1 or 2 grains or more (Lavater, *Pharm. Viertelj.* 2, 110). Larger doses of santonin, given to adults, produce colour-blindness lasting for several hours (Wells, *N. J. Pharm.* 15, 111; Martini, *Compt. rend.* 47, 259; 50, 545.— See also C. Rose, *Virchow's Arch. f. pathol. Anat.* 18, 15; 19, 522).

Santonin slowly turns yellow in diffused light, more quickly in direct sunshine. The crystals at the same time split into small irregular lumps (according to Heldt, first in fissures parallel to the principal axis), which are often scattered to a considerable distance. This action is exerted by the blue and violet, not by the yellow, green, or red rays. The change takes place also in the Torricellian vacuum, and under water, alcohol, ether, and oils (Trommsdorff). Lavorotatory power $[\alpha]j = -230°$ at 20° in alcoholic solution; weaker after addition of alkalis, not after addition of acids (Bucquet, *N. J. Pharm.* 40, 252). — Neutral (Kahler, Trommsdorff, Heldt); according to Ettling, it has an acid reaction.

				Liebig.	Ettling.	Heldt.
30 C		180	73·17	72·50	72·40	72·66
18 H		18	7·32	7 47	7·67	7·59
6 O		48	19·51	20 03	19·93	19 75
$C^{13}H^{15}O^6$.		246	100·00	100·00	100·00	100·00

Heldt analysed with accordant results:—*a.* santonin crystallised and dried over oil of vitriol; *b.* fused; *c.* crystallised from ether and dried at 100°; *d.* crystallised from boiling water and dried between paper; *e.* crystallised from acetic acid and dried over oil of vitriol.

Decompositions. 1. Fused santonin *heated* a little above the melting point, turns brown, gives off yellowish vapours (acid and irritating according to Wittstein), which flow back, condense to a yellow transparent resin, while the residue becomes carbonised (Trommsdorff). The yellow resin is insoluble in water, but dissolves in alcohol, ether, and alkalis, and in contact with the latter acquires a carmine-red colour, affording a delicate reaction. The yellow resin is likewise obtained by heating santonin with alkalis, alkaline earths, or metallic oxides. When kept for a long time, especially in solution, it loses the property of reddening with alkalis (Trommsdorff). — 2. Santonin heated in

contact with the air, *burns* with a yellow, very smoky flame (Tromms-dorff), white, with violet edges (Alms). — 3. *Phosphorus* thrown on melted santonin takes fire, turning the santonin brown, and partially converting it into a resin. — Santonin cannot be fused with *sulphur* (Trommsdorff). At higher temperatures, it decomposes in contact with sulphur, giving off hydrosulphuric acid (Heldt). — 4. When fused with *iodine*, it gives off hydriodic acid and iodine vapours, and is con-verted into a dark-coloured mass, which dissolves with cherry-red colour in alcohol. The alcoholic solution is coloured light-green by alkalis, and the alkaline solution is precipitated by nitric acid in red flocks, from which the admixed iodine may be extracted by ammonia. Iodine does not act on alcoholic santonin (Heldt). — 5. Santonin chars when *bromine* is poured upon it, giving off hydrobromic acid. Santonin immersed in water, or dissolved in hot alcohol, is converted by bromine into an orange-red resin; but when bromine is dropped into a cold dilute alcoholic solution of santonin, bromo santonin is produced (Heldt). — 6. Dry santonin is not altered when *chlorine gas* is passed over it; but melted santonin is converted into a brown resin, with evolution of hydrochloric acid. When chlorine is passed into water in which santonin is suspended, the santonin becomes covered with an opaque white crust. From a hot alcoholic solution of santonin, chlorine separates a yellowish-red oil, which solidifies to a resin on cooling (Trommsdorff, Heldt). — By heating santonin with *hydrochloric acid and chlorate of potash*, chloro-santonin is formed (Heldt). Santonin dissolves without colour in a large quantity of water, and the solution, after standing for a short time, deposits crystalline flocks (Willstein).

7. When santonin is heated with *glacial phosphoric acid*, a yellow liquid is formed, which solidifies to a yellow-brown resin, soluble in alcohol (Heldt). Santonin boiled continuously with aqueous phosphoric acid of sp. gr. 1·25, dissolves, and is partly precipitated by water in its original state. The yellow bitter solution boiled for some time, turns brown, and deposits a brown resin (Trommsdorff). Phosphoric acid resinises alcoholic santonin (Heldt). — 8. Santonin dissolves in *oil of vitriol*, quickly and without colouration, and is precipitated unaltered by water. The solution turns yellow on standing; then acquires a yellowish red colour (red, according to Heldt), extending from the surface downwards, and if the acid can absorb water, deposits cherry-red and brown-red resinous flocks, together with unaltered santonin. In a closed vessel, the solution acquires a dark brown colour, and is precipitated by water in red or brown flocks. When the santonin is heated with oil of vitriol, the same effects are produced, followed by carbonisation and separation of sulphurous acid (Trommsdorff). No conjugated acid appears to be formed by the action of oil of vitriol on santonin (Heldt). Oil of vitriol diluted with an equal quantity of water, resinises santonin when heated with it (Trommsdorff); dilute sulphuric acid digested with santonin, for some time forms a yellow oil, similar to that produced by hydrochloric acid (Heldt). — 9. *Hydrochloric acid* of sp. gr. 1·1, resinises santonin when boiled with it for some time (Trommsdorff). Warm concentrated hydrochloric acid dissolves it more readily than water, and on cooling deposits unaltered santonin ; after longer digestion, however, the solution deposits yellow oil-drops, which solidify to a red-brown resin, still mixed with unaltered santonin. From the decanted hydrochloric acid, water throws down white flocks,

and the solution filtered therefrom does not contain any sugar (Heldt). Hydrochloric acid gas passed into alcoholic santonin, does not form either a resin or a compound ether.

If, according to Kosmann (*N. J. Pharm.* 38, 81), santonin be boiled with dilute sulphuric acid, containing ⅓ of its weight of oil of vitriol, the boiling being continued for a time varying from four hours to a day, a quantity of resin (Kosmann's *santoniretin*) is separated, amounting to between 84 and 90 per cent. of the santonin, whilst sugar, or at least a body capable of reducing an alkaline cupric solution, remains dissolved. Kosmann suggests the equation:

$$C^{30}H^{18}O^6 + 4HO = \tfrac{1}{3} \, C^{12}H^{12}O^{12} + C^{26}H^{18}O^6.$$
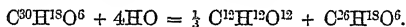
The formation of resin is more probably due to assumption of water, since santonin, which sublimes without alteration, can scarcely be a glucoside (Kr.).

10. Santonin dissolves in cold fuming *nitric acid;* in the more dilute acid only when heated, and is precipitated for the most part unaltered on diluting or cooling the solution (Trommsdorff, Heldt). By continued digestion with strong nitric acid, it is converted into an amorphous, sticky, bitter mass, which remains when the liquor is evaporated or is precipitated by water, as a white coagulum. This mass is free from nitrogen, precipitable from its alcoholic solution by neutral acetate of lead ; not precipitable by ammoniacal chloride of calcium. By the continued action of nitric acid, a bitter, amorphous mass is formed, easily soluble in water and precipitable by basic acetate of lead, and finally succinic acid, with evolution of hydrocyanic acid (Heldt). The bitter yellow solution formed, with evolution of nitrous gas, by boiling santonin with nitric acid, deposits white flocks when mixed with water, and contains oxalic acid (Trommsdorff). Santonin is oxidised by nitric acid to crystallisable *santonein*, which is insoluble in water, but dissolves in alcohol, and unites with alkalis (Phipson, *J. Pharm. d'Anvers*, 15, 112, and 213 ; *Pharm. Viertelj.* 8, 583. — 11. *Permanganate of potash*, either dissolved in pure water, or mixed with sulphuric acid, does not alter santonin, even at the boiling heat, not even in alcoholic solution (Heldt). — 12. From a mixture of *chromate of potash* and sulphuric acid, santonin, after long boiling, reduces a small quantity of chromic oxide. In a solution of santonin in oil of vitriol, bichromate of potash produces a brisk evolution of carbonic acid, which, however, soon ceases. Santonin takes fire when heated with dry chromic acid (Heldt). When bichromate of potash is added to a solution of santonin in oil of vitriol, yellow-brown zones are formed at first, the liquid afterwards assuming a yellow-green, and finally an emerald-green colour (Wittstein, *Pharm. Viertelj.* 6, 274). — 13. Santonin heated with *dry peroxide of lead*, detonates, and gives off a pungent vapour, which condenses to a mixture of resin and unaltered santonin. Santonin is not altered by digestion with peroxide of lead and dilute sulphuric acid (Heldt). —14. When it is dropped into melting *hydrate of potash*, the mass assumes a red colour, becoming darker as the heat increases, and gives off a large quantity of inflammable gas, probably hydrogen. The mass supersaturated with dilute sulphuric acid, yields a large quantity of resin or unaltered santonin, and a distillate containing formic, propionic, and perhaps also acetic acid (Banfi & Chiozza, *Ann. Pharm.* 91, 112 ; *J. pr. Chem.* 64, 357).

Combinations. Santonin dissolves in 4,000 to 5,000 pts. of cold, and

in 250 pts. of boiling *water* (Trommsdorff). In dilute *mineral acids* it does not dissolve more abundantly than in pure water. For its relations to concentrated acids, see pp. 252, 253.

Santonin unites with *bases*, without elimination of water. It decomposes alkaline carbonates, the carbonic acid not being expelled, but remaining to form an alkaline bicarbonate (Heldt); at the boiling heat it is given off (Hautz, *J. pr. Chem.* 62, 315).

The hot saturated aqueous solution of santonin does not precipitate any metallic salt (Trommsdorff). The compounds of santonin with the alkalis and alkaline earths are soluble in water; those with other metallic oxides are insoluble. These compounds are not altered by sunlight, or by the carbonic acid of the air, but they decompose for the most part when boiled with water or alcohol (Trommsdorff, Heldt). When mixed with mineral acids, they soon yield crystals of santonin. Acetic acid decomposes them with less facility, so that a dilute solution of the potassium-compound of santonin, mixed in the cold with acetic acid, does not deposit santonin till after several days (Trommsdorff). — If, when santonin is dissolved in aqueous alkalis or alkaline earths, a small quantity of alcohol be added to the solution, a bright carmine-red colour is produced, which gradually disappears in proportion as combination goes on; without addition of alcohol, this coloration does not take place (Trommsdorff). When santonin is fused with metallic oxides, the mass likewise assumes a red colour, but becomes colourless on addition of water (Heldt). Santonin which has become yellow by exposure to light, forms, when brought in contact with alkalis and alcohol, pure yellow solutions, or if colourless santonin is likewise present, purple-red solutions; the yellow solutions also slowly become colourless on standing. Yellow santonin, obtained in colourless crystals by re-crystallisation from alcohol, likewise assumes only a yellow colour in contact with alkalis; but the colourless crystals, separated from the alkaline solution by hydrochloric acid, turn red in contact with alcohol and potash-ley (Trommsdorff, Heldt).

Santonin heated with alcohol and *ammonia*, acquires a faint-red colour, and acids separate a small quantity of santonin from the filtrate. On boiling the solution, the dissolved santonin is precipitated, with evolution of ammonia (Tromsdorff). No compound of santonin with ammonia is formed under these circumstances (Heldt).

Potassium-compound of Santonin. —Santonin does not dissolve in cold potash-ley, but when boiled for some time with aqueous carbonate of potash, or caustic potash, it dissolves,—more easily, however, on addition of alcohol. The solution in caustic potash becomes turbid when evaporated, from separation of yellow oil-drops, which solidify to a soft amorphous mass soluble in water and alcohol, and are resolved by acids into santonin and a potash-salt (Trommsdorff).

To prepare the compound, santonin is boiled with aqueous alcohol and carbonate of potash, till the red colour produced at first has disappeared; the solution is evaporated to dryness at 37·5°; the residue is boiled with alcohol; and the solution again evaporated. — It is a white deliquescent gum, having a strong alkaline taste and reaction; melts to a dark red mass when heated, and leaves a large quantity of charcoal when ignited. It is decomposed by boiling with water, the solution yielding crystals of santonin. It dissolves readily in water, in alcohol, and in dilute, but not in concentrated potash-ley (Trommsdorff, Heldt).

Peretti (*N. J. Pharm.* 7. 373) describes a crystallisable compound of santonin and potash, also a compound of 2 at. santonin with 1 at. potash, both apparently containing free santonin (Ritter).

Sodium-compound. — Obtained in the same manner as the potassium-compound. Crystallises, by evaporation of the alcoholic solution, in slender interlaced needles ; by spontaneous evaporation of its aqueous solution, in large, transparent, colourless crystals, belonging to the right prismatic system (*Fig.* 55) $u : l = 119°\ 55'$ (obs.), $120°\ 32'$ (calc.) ; $u : u$ over $t = 118°\ 56'$ (calc.); $i : t = 109°\ 2'$ (obs.), $107°\ 51'$ (calc.); $i : i$ over $t = 142°\ 17'$ (obs.); $i : u = 99°\ 27'$ (obs.). Cleavable parallel to t (Weiss, *Wien. Akad. Ber.* 37, 377). Not altered by sunlight. Has an alkaline reaction. At 100°, it gives off 17·5° p. c. water (7 at = 18·05 p. c. HO), and at a higher temperature, 1 at. more, forming a carmine-red mass, which exhibits a glassy lustre when cold, becomes moist and glutinous on exposure to the air, and loses its colour on addition of water. — The compound yields by dry distillation a yellow-brown oil, which solidifies on cooling, and dissolves with carmine-red colour in alcoholic potash (Heldt).

	at 100°.			Heldt.
$C^{30}H^{18}O^6$	246	....	86·02	....
NaO	31	....	10·84	.... 10·46
HO	9	....	3·14	....
$C^{30}H^{18}O^6,NaO,HO$	286	....	100·00	....

The crystals contain 8·75 p. c. soda (Heldt), calc. = 8·66 p. c. NaO.

Barium-compound. — Obtained by digesting hydrate of baryta with alcoholic santonin, till the red colour disappears, then filtering, evaporating to dryness at 37·5°, exhausting with water, and again evaporating. — White, loosely coherent powder, having an alkaline taste and reaction (Heldt).

	at 120°.			Heldt.
$C^{30}H^{18}O^6$	246·0	....	72·23	....
BaO	76·6	....	22·49	.... 22·09
2HO	18·0	.... ..	5·28	....
$C^{30}H^{18}O^6,BaO,2HO$	340·6	....	100·00	....

Calcium-compound. — Santonin does not expel carbonic acid from carbonate of lime (Trommsdorff). The potassium-compound of santonin precipitates a strong solution of chloride of calcium. — Obtained like the barium-salt. The solution, when evaporated, yields crystalline crusts, which on drying, form white masses, having a silky lustre, not altered by exposure to air containing carbonic acid, or to sunlight. The compound has an alkaline taste and reaction. When heated, it acquires a ruby-red colour, and gives off a certain quantity of santonin. Soluble in water and in alcohol (Heldt).

	at 120°.			Heldt.]
$C^{30}H^{18}O^6$	246	....	86·93	... ...
CaO	28	....	9·89	.... 10.32
HO	9	....	3·18	....
$C^{30}H^{18}O^6,CaO,HO$	283	....	100·00	....

With 2 at. Santonin ? — When hydrate of lime is boiled with an

alcoholic solution of santonin, the liquid evaporated, the residue dissolved in water, carbonic acid gas passed into the filtrate as long as carbonate of lime is thereby separated, and the liquid again filtered and evaporated, long silky needles are obtained, having a slight alkaline reaction, and faintly saline bitter taste.   These crystals dissolve in water and in dilute alcohol, less freely in strong alcohol, and are decomposed by boiling with water (Trommsdorff).   These needles appear to be identical with the calcium-compound of santonin, analysed by Laubenheimer (*Ann. Pharm.* 11, 208), who found in it 5·09 p. c., corresponding nearly to the formula $2C^{30}H^{18}O^6$,CaO, which requires 5·39 p. c. CaO (Heldt).

Magnesium-compound. — The aqueous solution of the potassium-compound of santonin does not precipitate sulphate of magnesia. Santonin boiled with magnesia and alcohol acquires a faint red colour. On evaporating and exhausting the residue with water, a solution is obtained, from which acids precipitate santonin.

Aluminium-compound. — From the aqueous solution of the potassium-salt, sulphate of alumina throws down a white precipitate, which dissolves in excess of the precipitant.   The latter solution becomes turbid when heated, from separation of alumina and santonin.—The compound forms white flocks, which melt without reddening when heated. Soluble in alcohol (Trommsdorff).

The potassium-compound throws down from *uranic salts*, a yellow precipitate ; from *chromic salts*, a green precipitate (Heldt). — From a strong solution of *sulphate of zinc*, it precipitates white flocks, which dissolve readily in water, are decomposed by boiling with it, and melt to a red mass when heated.   Soluble in alcohol (Trommsdorff).

Lead-compound. — From the aqueous solution of the potassium-compound, neutral acetate of lead throws down white flocks, which crystallise from water or alcohol in needles having a silky lustre (Trommsdorff).   When a hot aqueous solution of neutral acetate of lead is mixed with a boiling alcoholic solution of santonin, and the filtered liquid is kept at a temperature between 40° and 50°, it deposits nodules consisting of small needle-shaped crystals having a pearly lustre ; after prolonged washing, they contain 33·7 p. c. lead-oxide, and decompose partially when recrystallised from alcohol.   The mono-santonin-compound, containing 31·18 p. c. PbO (calc. for $C^{30}H^{18}O^6$,PbO = 31·25 p. c.) is obtained by precipitating a solution of neutral acetate of lead with santonin, washing the precipitate, and drying it at 100°. When heated, it assumes a carmine colour and gives off water (Heldt). It is decomposed by prolonged boiling with water.   When boiled with excess of neutral acetate of lead, it dissolves, with formation of basic acetate of lead (Trommsdorff).

The potassium-compound of santonin forms with *ferrous sulphate*, a white precipitate ; with *ferric chloride*, yellow flocks which dissolve in excess of the iron-salt, and in alcohol ; the alcoholic solution deposits flocks of ferric oxide when heated (Trommsdorff).

Copper-compound. — Precipitated from a concentrated solution of the potassium-salt by cupric sulphate, in pale-blue flocks, which dissolve in water and in alcohol, and are decomposed by boiling the solution (Trommsdorff).

Mercurous compound. — Mercurous nitrate forms with the potassium-compound of santonin a white precipitate, which, when boiled with water, yields mercurous oxide and santonin. The mercurous compound is soluble in alcohol (Trommsdorff). The white precipitate produced on mixing mercurous nitrate and the sodium-compound of santonin, is inodorous, insoluble in water and alcohol, and not decomposed by boiling water (*N. Br. Arch.* 100, 147).

Mercuric compound. — A dilute solution of the potassium-compound is not precipitated by mercuric chloride; but in a concentrated solution a white precipitate is formed, very soluble in water and in alcohol, and decomposed by prolonged boiling of its solution (Trommsdorff).

Silver-compound. — The potassium-compound throws down from nitrate of silver a white precipitate, soluble in water and in alcohol. The aqueous solution, when heated, deposits oxide of silver (Trommsdorff).

Santonin dissolves at 17·5° in 43 pts. *alcohol* of sp. gr. 0·848; at 50° in 12 pts.; at 80° in 2·7 pts. In alcohol of sp. gr. 0·928 it dissolves at 17·5° in 280 pts., and at 83·8° in 10 pts. (Trommsdorff). The solution of yellow santonin in alcohol becomes colourless when excluded from the air, and deposits colourless santonin, which, however, exhibits the reaction of yellow santonin with potash and alcohol (p. 254) (Trommsdorff, Heldt). — Santonin dissolves in 72 pts. of cold and 42 pts. of boiling *ether* (Trommsdorff). — It dissolves in 4·35 pts. of *chloroform*. Santonin which has become yellow by exposure to light, dissolves more abundantly, viz. in 3 pts. of chloroform, and the solution, which is yellow at first, becomes colourless in time, and if then evaporated at a comparatively low temperature, deposits colourless crystals, whereas, if evaporated by heat, it yields yellow crystals (Schlimpert, *N. Br. Arch.* 100, 151).

Santonin dissolves easily in *acetic acid* (Alms); the acid of sp. gr. 1·073 dissolves it, even in the cold; weaker acid only when warmed (Trommsdorff). Concentrated aqueous *tartaric acid* dissolves only traces of santonin (Riegel, *N. Br. Arch.* 58, 277). — Santonin dissolves in *volatile oils* (Alms), in gently warmed oil of turpentine (Kahler). According to Alms and Kahler, it is insoluble in *fixed oils;* but according to Trommsdorff, it dissolves abundantly in warm olive oil, crystallising out for the most part on cooling, and unites in all proportions with hot olive-oil. — *Infusion of galls* added to a hot aqueous solution of santonin, throws down, on cooling, yellow flocks soluble in alcohol (Trommsdorff).

Chlorosantonin.

$$C^{30}Cl^2H^{16}O^6 = C^{30}Cl^2H^{16}O^2,O^4.$$
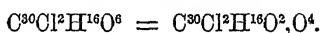
Heldt. *Ann. Pharm.* 63, 32.

Santonin is dissolved in a warm mixture of hydrochloric acid with a small quantity of alcohol, and small crystals of chlorate of potash are added, the liquid being frequently stirred and kept warm. After some time, the whole of the chlorosantonin separates on the surface

as a white amorphous mass, which must be washed for some time with water, and dissolved in hot absolute alcohol. The solution, when abandoned to spontaneous evaporation, yields white needles, an additional quantity of which may be obtained from the mother-liquor. The same solution evaporated by heat, deposits an orange-red resin, identical with that which is produced by chlorine in a hot alcoholic solution of santonin.

Properties. White, shining, delicate needles, not altered by exposure to daylight or to the air. Grates between the teeth. Melts when heated to a yellowish liquid, which solidifies again on cooling. Inodorous and tasteless in the solid state, but very bitter when dissolved in alcohol (Neutral).

		at 100°.			Heldt. *mean.*
30	C	180	57 14		56·85
2	Cl	71	22·54		21·94
16	H	16	5·08		5 50
6	O	48	15·24		15·71
C^{30}Cl^{2}H^{16}O^6		315	100 00		100 00

Decompositions. Chlorosantonin, *heated* above its melting point, is decomposed, with evolution of hydrochloric acid. — When exposed to *sunlight*, even in an atmosphere of hydrogen, it turns red, and afterwards brown, by superficial resination, but not so quickly as santonin. Hydrochloric acid is set free at the same time. Alcohol removes from the coloured product the brown crust, and leaves white crystals. *Ammonia-gas* does not act on chlorosantonin moistened with alcohol, or on the hot alcoholic solution. — Chlorosantonin dissolves in alcoholic *potash*, forming an orange-red liquid, which, on evaporation, yields orange-red drops of a potash-compound, becoming indigo-blue when heated for a longer time. If the potash be removed by sulphuric acid, and the excess of that acid by carbonate of baryta, the filtrate then evaporated over the water-bath, and the dry residue exhausted with absolute alcohol, a red filtrate is obtained, which leaves a red resin when evaporated. This resin dissolves in alcohol and in ether, is precipitated milky by water, and cakes together when the turbid liquid is heated.

Chlorosantonin is insoluble in *water*, but dissolves easily in *alcohol* and in *ether*. The alcoholic solution is precipitated by water, and afterwards becomes clear, yielding needle-shaped crystals at the same time.

Bromosantonin.

HELDT. *Ann. Pharm.* 63, 36.

Bromine is dropped gradually into a cooled alcoholic solution of santonin, and the liquid is left to evaporate; it then deposits an orange-brown resin and crystals.

White crystals, resembling chlorosantonin. Inodorous. Tasteless.

The crystals, dried over oil of vitriol, gradually turn yellow and then red when exposed to sunlight, giving off hydrobromic acid at the same time. If they still retain a trace of alcohol, they decompose

even when kept in the dark, becoming covered with a dark, purple-red crust, soluble in alcohol. — They turn red-brown even at 100°, and melt, when heated, to a cherry-red liquid, which does not recrystallise on cooling. — They dissolve in alcoholic potash, forming a cherry-red liquid.

Bromosantonin dissolves with difficulty in *water*, more readily in boiling *alcohol* and in *ether*.

Oxygen-nucleus $C^{30}H^{14}O^6$.

Santalic Acid.

$$C^{30}H^{14}O^{10} = C^{30}H^{14}O^6,O^4.$$
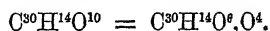
PELLETIER. *J. Phys.* 79, 268; *Bull. Pharm.* 6, 434. — *Ann. Chim. Phys.* 51, 193; *Ann. Pharm.* 6, 48; *Schw.* 67, 88.

VOGEL. *Ann. Pharm.* 6, 38.

BOLLEY. *Ann. Pharm.* 62, 150; abstr. *Pharm. Centr.* 1847, 650; *J. pr. Chem.* 43, 510.

L. MEIER. *N. Br. Arch.* 55, 285 and 56, 41; abstr. *Pharm. Centr.* 1849, 97; *Chem. Gaz.* 1849, 130; *Ann. Pharm.* 72, 320.

WEYERMANN & HAFFELY. *Ann. Pharm.* 74, 226; abstr. *Pharm. Centr.* 1850, 797; *Chem. Gaz.* 1850, 353.

Sandal-red. Santalin. The colouring matter of red sandal-wood, *Pterocarpus santalinus* and *Pt. indicus* (*Handbuch* viii., *Phytochem.* 12.)— For Preisser's statements, which are not confirmed by Bolley, see *Rev. scient.* 16, 49; *J. pr. Chem.* 32, 145. — Meier found in sandal-wood, besides santalic acid, five different bodies, which he designates as *Santalic oxide, Santalide, Santaloïde, Santalidide,* and *Santaloïlide;* but the separate existence and the purity of these bodies appear doubtful. Weyermann & Haffely were not able to find Meyer's santalic oxide.

Preparation. Rasped sandal-wood is exhausted with alcohol; the solution is evaporated; the resinous residue is boiled with water and redissolved in alcohol; the tincture is precipitated with an alcoholic solution of neutral acetate of lead; and the dark violet precipitate is collected, boiled repeatedly with alcohol of 80 p. c., and decomposed, either with alcohol containing sulphuric acid, or by treatment with hydrosulphuric acid. The santalic acid is obtained by evaporating the solution (Meier). The product is purified from mineral salts by mixing the alcoholic solution with a small quantity of hydrochloric acid, precipitating with water, and recrystallising from alcohol (Weyermann & Haffely). The ethereal or alcoholic extract may also be exhausted by boiling with water, santalic acid then remaining (Meier). Pelletier's sandal-red is obtained by evaporating the alcoholic tincture. Bolley exhausts with alcohol, distils off the greater part of the alcohol, and precipitates the colouring matter with water. Or he exhausts with dilute potash, precipitates with hydrochloric acid, dissolves the washed precipitate in alcohol, and reprecipitates with water.

Properties. Very small, microscopic prisms of a fine red colour, without taste or smell. Melts at 104°. Permanent in the air. Has an acid reaction (Meier).

| at 100°. | | Bolley. mean. | | Weyermann & Haffely. |
		a.	b.	mean.
30 C 180	.... 65·69	.... 64·45	.... 65·73	.... 65·85
14 H 14	.... 5·11	.... 5·07	.... 5·49	.... 5·20
10 O 80	.... 29 20	... 30·48	.... 28·78	.... 28·95
$C^{30}H^{14}O^{10}$ 274	.... 100·00	.... 100·00	.... 100·00	.... 100·00

Bolley analysed santalic acid (*a*), precipitated from the alkaline solution by hydrochloric acid, and (*b*) from the alcoholic solution by water. In impure santalic acid, Pelletier found 74·7 p. c. C., 6·4 H., and 18·9 O.

Decompositions. 1. When *heated* above its melting point, it swells up, takes fire, and burns with a bright white flame and agreeable odour (Meier). — 2. A mixture of 2 pts. of a concentrated alcoholic solution of santalic acid and 1 pt. strong nitric acid, assumes a brown colour when boiled, but does not give off any red fumes, even when evaporated. Water separates from the residue a yellow-brown powder, soluble in alcohol ; the acid filtrate, neutralised with carbonate of baryta, yields nitrate of baryta and yellow crystals of a deliquescent baryta-salt (Meier). Pelletier's sandal-red is decomposed by cold, and more quickly by hot nitric acid, into a yellow bitter resin, dissolved artificial bitter, and a large quantity of oxalic acid. — 3. The solution of santalic acid in *oil of vitriol* blackens when heated; water throws down from it a black, amorphous mass, which dissolves in boiling potash-ley, is precipitated by acids, and is resolved by alcohol into santalic acid, which dissolves, and a residue of charcoal. Alcoholic santalic acid is not altered by boiling with dilute acids (Meier). — 4. The acid mixed with alcoholic *nitrate of silver* turns brown on boiling, and deposits a brown powder (Meier). — 5. When santalic acid is kept for several days at 100° in contact with strong aqueous *ammonia,* and excluded from the air, it takes up ammonia, which it does not give up to acids, or when heated with hydrate of lime, but only when melted with sticks of potash (Schützenberger, *Zeitschr. Chem. Pharm.* 4, 65).

Combinations. Santalic acid does not dissolve in *water* either cold or boiling. It dissolves in *oil of vitriol* with dark red colour, and is precipitated by water (Meier).

Santalic acid neutralises bases, and unites with them, forming uncrystallisable *salts ;* those which are soluble have a slightly astringent taste. The acid dissolves readily in aqueous ammonia, and in aqueous solutions of the fixed alkalis. Its solution boiled with metallic oxides, forms red lakes, the colour of which is not extracted by alcohol (Meier).

The solution of santalic acid in aqueous *ammonia* is violet-red, and leaves, when evaporated, a residue free from ammonia (Meier).

Santalate of Potash. — Obtained by neutralising the acid with potash-ley. Amorphous, dark violet mass. Permanent in the air. It dissolves easily in water, with fine violet colour, changing to red on dilution. It is sparingly soluble in absolute alcohol.

Santalate of Soda. — Separates as a dark violet powder on neutralising a concentrated alcoholic solution of santalic acid with caustic

soda. It is not crystallisable, dissolves easily in water, but is insoluble in alcohol and in ether (Meier).

Santalate of Baryta. — An alcoholic solution of santalic acid does not precipitate chloride of barium, but on saturating it with baryta-water, a violet-blue powder is obtained, sparingly soluble in cold water, more easily in boiling water, insoluble in alcohol and ether (Meier). — To prepare the salt, santalate of ammonia is precipitated with chloride of barium, and the dark violet crystalline salt is washed out of contact with the air (Weyermann & Häffely).

		at 100°.				Weyermann & Häffely. mean.
30	C	180·0	....	52·7	....	53·45
13	H	13·0	....	3·8°	....	4·05
9	O	72·0	....	21·1	....	19·60
	BaO	76·5	....	22·4	....	22·90
$C^{30}H^{13}BaO^{10}$		341·5	......	100·0	....	100·00

In the calculation it is assumed that the baryta remained after the combustion as mono-carbonate.

Santalate of Lime. — Precipitated by lime-water from the alcoholic solution of the acid. Dark, violet mass, nearly insoluble in water.

The compounds of santalic acid with *magnesia, alumina, zinc-oxide, stannous, ferrous, ferric,* and *cupric oxides,* are obtained from the potash-salt by double decomposition, as violet precipitates insoluble in water, alcohol, and ether (Meier).

Santalate of Lead. — Obtained by precipitating alcoholic santalic acid with neutral alcoholic acetate of lead, washing the precipitate with alcohol, and drying it at 100° (Weyermann & Häffely).

						Weyermann & Häffely. mean.
30	C	180·0	....	36·2	....	36·15
14	H	14·0	....	2·8	....	2·80
10	O	80·0	....	16·5	....	16·30
2	PbO	223·2	....	44·5	.. ....	44·75
$C^{30}H^{14}O^{10},2PbO$		497·2	....	100·0	....	100·00

Bolley analysed a lead-salt containing from 31·38 to 32·18 p. c. lead-oxide.

Santalate of Silver. — Thrown down by the potash-salt from nitrate of silver as a brown precipitate (Meier).

Santalic acid dissolves, with blood-red colour and in all proportions, in absolute *alcohol* and in spirit of 80 p. c.; in spirit of 60 p. c. only when warmed (Meier). It dissolves readily in *acetic acid,* and is precipitated from the concentrated solution by water (Pelletier, Meier).

Santalic acid is soluble in *ether.* The solution is not red, like the alcoholic, but yellow (according to Meier, it does not redden litmus); when quickly evaporated in vacuo, it often leaves the acid quite yellow, and when evaporated in contact with the air, of a fine red colour

(Pelletier). — It dissolves in certain *volatile oils* (viz., the oils of berga-mot, cinnamon, bitter almond, clove, and rose), in others only partially, and in others (viz., turpentine, anise, and lemon) not at all (Voget, Meier). It dissolves with difficulty in the oils of *linseed, olive,* and *rape,* not in oil of almonds (Meier).

<center>*Oxygen-nucleus* $C^{30}H^{10}O^{10}$.</center>

Datiscetin.

$$C^{30}H^{10}O^{12} = C^{30}H^{10}O^{10},O^{2}.$$
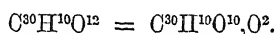
Stenhouse. *Ann. Pharm.* 98, 170; abstr. *Chem. Soc. Qu. J.* 9, 226; *N. Phil. Mag. J.,* 12, 59; *J. pr. Chem.* 68, 36; *N. J. Pharm.* 30, 326.

Formation and Preparation. A. *From Datiscin.* 1. Datiscin is boiled with dilute sulphuric acid, and the datiscetin, which separates after some minutes, is collected:

$$C^{42}H^{22}O^{24} = C^{30}H^{10}O^{12} + C^{12}H^{12}O^{12}.$$
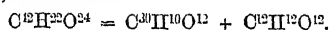
2. By boiling diatiscin with potash, and precipitating with an acid.— B. *From the mother-liquors obtained in the preparation of datiscin.* — These liquors are precipitated with basic acetate of lead: the precipitate is decomposed under water by hydrosulphuric acid; and the concentrated filtrate is boiled with dilute sulphuric acid; a resin then separates at the bottom, and the liquid decanted therefrom yields diatiscetin on further boiling. The product is purified by solution in alcohol and precipitation by water.

Properties. Nearly colourless needles, which melt when heated, and solidify in the crystalline form on cooling. Tasteless.

		at 100°.			Stenhouse. mean.
30	C	180		62·94	62·92
10	H	10		3·49	3·66
12	O	96		33·57	33·42
$C^{30}H^{10}O^{12}$		286		100·00	100·00

Decompositions. 1. Datiscetin very cautiously heated, yields a crystalline sublimate, which tastes sweet when re-crystallised from ether. — 2. When heated it *burns,* without any odour of burnt sugar. — 3. Cold *nitric acid* converts it, with rise of temperature and evolution of brown vapours, into a resin, which then dissolves to a dark red liquid, and when boiled and evaporated, leaves picric acid. No oxalic acid is produced in this reaction. Datiscetin boiled with dilute nitric acid, yields nitrosalicylic acid. — 4. With melting *hydrate of potash,* it acquires an orange-colour, and gives off hydrogen. The residue treated with hydrochloric acid, yields a resin and salicylic acid. — 5. When distilled with *bichromate of potash* and dilute sulphuric, it yields a watery distillate, which smells of salicylous acid, and reddens ferric salts.

Combinations. Datiscetin is nearly insoluble in *water*. It dissolves in aqueous *alkalis*, and is precipitated by acids.

Lead-compound. By mixing an alcoholic solution of datiscetin with neutral acetate of lead, a deep yellow precipitate is obtained, which may be washed with alcohol and water.

				Stenhouse. mean.
30 C	180·0	36·63	36·10
8 H	8·0	1·63	1·65
10 O	80·0	16·28	16·89
2 PbO	223·4	45·46	45·36
$C^{30}H^8Pb^2O^{12}$	491·4	100·00	100·00

Datiscetin dissolves easily in *alcohol*, and in nearly all proportions in *ether*.

Glucosides of Datiscetin.

Datiscin.

$$C^{42}H^{22}O^{24} = C^{30}H^{10}O^{12}, C^{12}H^{12}O^{12}.$$
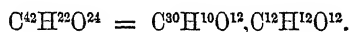
BRACONNOT. *Ann. Chim. Phys.* 3, 277.
STENHOUSE. *Ann Pharm.* 98, 166; abstr. *Chem. Soc. Qu. J.* 9, 226; *N. Phil. Mag. J.* 12, 59; *J. pr. Chem.* 68, 36; *N. J. Pharm.* 30, 236.

Occurrence. In the herb and roots of *Datisca cannabina* (*Handbuch.* viii., *Phytochem.* 32).

Preparation. The comminuted roots are exhausted with wood-spirit; the mother-liquors are evaporated to a syrup; the resins contained in them are precipitated by addition of ½ volume hot water; and the decanted liquid is evaporated to the crystallising point. The impure datiscin thus obtained is purified by pressing it, mixing the alcoholic solution with water, and filtering the liquid from the resin which is precipitated on evaporation. The mother-liquors serve for the preparation of datiscetin (Stenhouse). Braconnot obtained datiscin by evaporating the decoction, or by treating the extract with cold water, and re-crystallising the insoluble deposits from boiling water.

Properties. Colourless needles or laminæ, having a silky lustre, soft and translucent, like grape-sugar. Yellowish, if not quite pure. Neutral.

	Needles.			Stenhouse. mean.
42 C	252	54·08	54·57
22 H	22	4·72	5·21
24 O	192	41·20	40·22
$C^{42}H^{22}O^{24}$	466	100·00	100·00

Some of the specimens of datiscin analysed by Stenhouse, still contained ash.

Decompositions. 1. Datiscin melts at 180°, burns when further *heated*, emitting an odour of burnt sugar, and leaves charcoal. Heated in a current of dry air, it yields a small quantity of crystalline sublimate, probably datiscetin. — 2. When boiled with dilute *sulphuric* or *hydrochloric acid*, and more slowly by boiling its aqueous solution, it is resolved into datiscetin and sugar:

$$C^{42}H^{22}O^{24} = C^{30}H^{10}O^{12} + C^{12}H^{12}O^{12}.$$
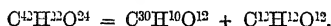
The sugar obtained from 100 pts. of datiscin reduces as much cupric oxide from alkaline solution as 37·8 to 41·6 pts. of common sugar (calc. 38·6 pts.) (Stenhouse). — 3. *Nitric acid* gradually dissolves datiscin, forming a yellow solution, which, when evaporated, leaves oxalic and picric acids. — 4 By boiling with strong *potash-ley*, it is decomposed in the same manner as by acids. — 5. It is not altered by contact with *yeast* or *emulsin.*

Datiscin is slightly soluble in cold, more abundantly in hot *water.* — According to Braconnot, it dissolves in *oil of vitriol*, and is precipitated by water and by ammonia, but is nearly insoluble in hydrochloric acid (vid. sup.). With *iodine*, it forms a yellow compound, soluble in cold water (Braconnot).

Datiscin forms with aqueous *ammonia* and the *fixed alkalis*, deep yellow solutions, which are precipitated and decolorised by acids. — Aqueous datiscin forms with *neutral* and *basic acetate of lead*, a light yellow gelatinous precipitate; with ferric salts, a dark green; with copper-salts a greenish; and with *stannic chloride*, a light yellow precipitate (Stenhouse). It is not precipitated by *tincture of galls* (Braconnot), or by solution of *gelatin* (Stenhouse).

Datiscin dissolves easily in cold *alcohol*, and in all proportions in boiling alcohol; sparingly in *ether* (Stenhouse). It dyes fabrics both mordanted and unmordanted (Bracannot).

Primary Nucleus $C^{30}H^{22}$; *Oxygen-nucleus* $C^{30}H^{20}O^2$.

Pipitzahoic Acid.

$$C^{30}H^{20}O^6 = C^{30}H^{20}O^2,O^4.$$
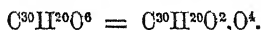
M. C. WELD. *Ann. Pharm.* 95, 188; abstr. *J. pr. Chem.* 66, 375; *Pharm. Centr.* 1855, 800.

Riozolic acid. Discovered by Rio de la Loza, in the root called *Raiz del Pipitzahuac*, which, according to Ramon de la Sagra, belongs to the synanthareous plant *Dumerilia Humboldtia* of Toluca (see *Compt. rend.* 42, 873, and 1072).

It is obtained in an impure state, by dry distillation of the root, better by exhaustion with alcohol and crystallisation, and purified by recrystallisation from absolute alcohol.

Properties. Gold-coloured tufts of laminar crystals. From ether it separates in small shining tables belonging to the oblique prismatic system. Oblique rhombic prism u (*Fig.* 91) of 84° and 96°, and having

the end-face *i* inclined to the prismatic faces at an angle of 94°. Permanent in the air. Melts at about 100° to a red liquid, which solidifies in the crystalline form on cooling, and sublimes at a temperature a little above 100° in gold-yellow laminæ.

					Weld.		
30	C	180	72·58	72·04	to	73·24
20	H	20	8·06	7·94	....	8·40
6	O	48	19·36	20·02	...	18·36
$C^{30}H^{30}O^6$		248	100·00	100·00	....	100·00

Combinations. Nearly insoluble in *water*. — Unites with *bases*, forming salts. *Caustic alkalis* and *alkaline carbonates* colour the solutions of the acid purple-red, and form salts easily soluble in water, alcohol, and ether, which remain as varnishes on evaporation, and are decomposed in alcoholic solution by carbonic acid.

Baryta-salt. — Baryta-water throws down from the alcoholic solution of the acid, dark purple grains, sparingly soluble in water and in alcohol. It is decomposed by carbonic acid in alcoholic solution.

Copper-salt. — Obtained by precipitating the soda-salt with acetate of copper, dissolving the precipitate in alcohol, precipitating with water, washing, and drying over oil of vitriol. — Dark greenish brown, non-crystalline mass. Contain 6·84 p. c. hydrogen, and 11·12 p. c. copper, and is therefore $C^{30}H^{19}CuO^6$ (calc. 6·81 H., and 11·36 Cu). — Melts above 100°, depositing cupric oxide, while part of the acid sublimes. Soluble in alcohol and in ether.

Lead-salt. Obtained by precipitating the soda-salt with basic acetate of lead, and dissolving the precipitate in alcohol. Contains 44·02 p. c. lead, and is therefore perhaps $\dot{C}^{30}H^{18}Pb^2O^6$ (calc. 45·7 p. c. lead).

Silver-salt. Obtained by precipitating the soda-salt with nitrate of silver, as a dark purple precipitate, insoluble in water, soluble in alcohol and ether. Contains 29·35 p. c. silver ($C^{30}H^{19}AgO^6 = 30·42$ p. c. Ag.)

The acid dissolves easily in *alcohol* and *ether*, and is precipitated by water.

Oxygen-nucleus $C^{30}H^{12}O^{10}$.

Anemonin.

$$C^{30}H^{12}O^{12} = C^{12}H^{12}O^{10}, O^2.$$
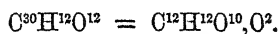
HEYER. *Crell. Chem. J.* 2, 102.—*Crell. N. Entd.* 4, 42.
VAUQUELIN & ROBERT. *J. Pharm.* 6, 229; *N. Tr.* 1, 365.
J. SCHWARZ. *Mag. Pharm.* 10, 193; 19, 168.
RABENHORST. *N. Br. Arch.* 27, 93.
LÖWIG & WEIDMANN. *Pogg.* 46, 45; *Ann. Pharm* 32, 276.
FEHLING. *Ann. Pharm.* 38, 278.
JUL. MÜLLER. *N. Br. Arch.* 63, 1; *Pharm. Centr.* 1850, 618.
O. L. ERDMANN. *J. pr. Chem.* 75, 209; *Rép. Chim. pure* 1, 192.

Anemony-camphor. Pulsatilla-camphor. Anemoneum. First observed by Störk (*Libellus de usu med. Pulsatillæ nigric.* Wien. 1771); re-discovered by Heyer in 1779. — The volatile acrid principles (xiv. 471) are perhaps related to the body from which anemonin and anemonic acid are formed.

Occurrence and Formation. The fresh herb of *Anemone pratensis, A. Pulsatilla* (Heyer), and *A. nemorosa* (Schwarz), of *Ranunculus Flammula, R. bulbosus* (J. Müller), and *R. sceleratus* (Erdmann), yields, by distillation with water, a clear distillate, having a sharp taste, and pungent, tear-exciting odour. This liquid yields to ether an acrid oil, which, according to Schwarz and Erdmann, does not redden litmus, but, according to Muller, has a strong acid reaction. It has a golden-yellow colour, is heavier than water, free from sulphur, and decomposes by keeping, or in contact with water or chloride of calcium, into anemonin and anemonic acid (Erdmann). The water distilled over the anemony plant, especially if concentrated by cohobation, likewise deposits, after keeping for some weeks or months, crystals of anemonin and white pulverulent anemonic acid, separable by alcohol, which dissolves only the crystals. This treatment deprives the anemonin of its acridity (Heyer, Schwarz).

Properties. Colourless, shining prisms belonging to the right prismatic system. The crystals, which are mostly tabular, exhibit all the faces of Fig. 53, with this difference, that neither i nor u truncates symetrically the edges of the octahedron α; between p and y there is a prism s; also an octahedron β, situated in the same zones with p and α, also with t and s. The more simple crystals exhibit only the faces $t, i, p,$ and $u.$ — $m : u = 148°\ 30'$ (nearly); $m : y = 130°\ 0'$; $p : i = 115°\ 19'$; $p : s = 157°\ 13'$; $p : \alpha = 126°\ 37'$; $p : \beta = 146°\ 2'$; $y : s = 152°\ 43'$; $\alpha : \beta = 160°\ 15'$. The t-face is striated parallel to i (Grailich & Lang, *Wien. Akad. Ber.* 27, 60). Different from these are the crystals obtained by Frankenheim (*N. Br. Arch.* 63, 3): 1. From *Pulsatilla pratensis.* Short rhombic prisms y (*Fig. 53*), having their lateral edges truncated by p and m, acuminated at the top by i and u. Subordinate are two octahedrons, the lower being that whose edges are symmetrically truncated by i, u, y; also a truncation between y and m. Cleavage-planes parallel to m and p: $u : m = 112°\ 15'$; $i : p = 130°\ 34'$. — 2. From *Anemone nemorosa.* Long prisms, with predominating faces m, y; also u, a truncating face between u and m, another between y and m, and lastly, the end-face t.

Heavier than water. Very friable. Inodorous. In the solid state it has little more than a fatty taste, but in the melted state its taste is intensely biting and burning, and leaves a numbness on the tongue for several days (Heyer, Robert). It is an acrid poison. — Neutral to vegetable colours (Fehling).

		Crystals.		Lowig & Weidmann. mean.		Fehling. mean.
30 C	180	....	62·50	....	54·69	.... 62·45
12 H	12	....	4·17	....	4·30	.... 4·29
12 O	96	....	33·33	....	41·01	.... 33·26
$C^{30}H^{12}O^{12}$	288	....	100·00	....	100·00	.... 100·00

Lowig & Weidmann gave the formula $C^7H^5O^4$. The discrepancies of their analyses have not been explained.

Decompositions. 1. Anemonin softens at 15°, giving off water and a very pungent vapour; the yellow residue decomposes above 300°, with separation of charcoal (Fehling). — According to earlier observations. anemonin is volatile. — By dry distillation, it yields a limpid watery distillate, having a peppery taste, also a yellow empyreumatic sublimate, soluble in alcohol, and a residue of charcoal (Heyer). When it is heated in a glass tube, the greater part volatilises undecomposed, and condenses to a solidifying oil, a small quantity of brown resin remaining behind (Vauquelin). — 2. When held in a lamp-flame, it burns away completely, with a bright flame (Heyer). It dissolves without decomposition in cold *oil of vitriol* (Löwig & Weidmann), the solution not blackening, even after many days (Müller). According to Fehling, it is carbonised by oil of vitriol. — 4. When quickly heated in *chlorine gas*, it gives off a large quantity of hydrochloric acid, and forms a yellow volatile oil (Fehling). — 5. Strong *hydrochloric* acid converts it into anemoninic acid (Löwig & Weidmann). — 6. Heated with *nitric* acid, it forms oxalic acid (Fehling). — 7. Heated with *peroxide of manganese* and *sulphuric acid*, it yields formic acid (Fehling).

8. It dissolves without decomposition in aqueous *alkalis* and in *baryta-water* (Fehling); according to Lowig & Weidmann, however, it takes up at the same time 2 at. water, and is converted into their *anemoninic acid*.

a. *According to Lowig & Weidmann.*—When anemonin is boiled with excess of concentrated baryta-water, red flocks of basic anemoninate of baryta are deposited, which dissolve with yellow colour on addition of a large quantity of anemonin. If the basic salt is converted into a neutral salt by passing carbonic acid into the liquid, the neutral salt precipitated by neutral acetate of lead, the lead-salt decomposed by hydrosulphuric acid, and the filtrate evaporated, anemonin remains as an amorphous, brittle, translucent brown mass, which melts at 100°, dissolves easily in water, sparingly in alcohol, and not at all in ether. This acid, according to Lowig & Weidmann, is $C^7H^5O^6$, contains 43 p. c. C., and 5·1 H., and forms with bases, brown amorphous salts, of which the lead-, mercury-, and silver-salts are insoluble in water.

b. *According to Fehling.* Anemonin dissolves in aqueous alkalis, with yellow colour, neutralising them completely, and the solutions, when evaporated, leave a brown mass, from which acids separate a yellow gum easily soluble in water. — When anemonin is dissolved in baryta-water, and carbonic acid is passed into the slightly alkaline liquid, a small quantity of organic substance is precipitated together with the carbonate of baryta. This organic substance, which remains in solution after the precipitate has been dissolved in acetic acid, and the baryta precipitated by sulphuric acid, is yellow, crystalline, and does not precipitate ammoniacal solutions of lead- or silver-salts. — The solution of anemonin in baryta-water, when freed from carbonate of baryta and excess of carbonic acid, and then mixed with neutral acetate of lead, yields a light yellow precipitate, which contains 26·64 p. c. C., 2·19 H., 16·42 O., and 54·75 PbO., agreeing nearly with the formula $C^9H^4O^4$. The quantity of this precipitate amounts to scarcely $\frac{7}{10}$ of the anemonin employed; hence the acid cannot be formed from anemonin by simple assumption of water (Fehling).

Compounds of Anemonin.   Anemonin is very slightly soluble in cold *water*; from solution in boiling water it crystallises on cooling (Vauquelin).

It unites with *lead-oxide* and *silver-oxide* (Fehling).

Lead-compound. — Obtained by boiling anemonin and lead-oxide with *water*, and crystallises from the filtrate on cooling, together with anemonin, which may be extracted by hot alcohol. The hot filtrate treated with alcohol, yields a precipitate containing 60·28 p. c. oxide of lead (Fehling).

					Fehling.
30 C	....	180	......	35·15	35·63
12 H	....	12	......	2·34	2·68
12 O	....	96	......	18·76	18·94
2 PbO	....	224	......	43·75	42 75
$C^{30}H^{12}O^{12}$,2PbO	.....	512	......	100·00	100·00

Silver-compound. — Crystallises from the hot-filtered solution obtained by boiling anemonin with carbonate of silver (Fehling).

Anemonin dissolves sparingly in cold, easily in boiling *alcohol,* and crystallises on cooling. — It is insoluble in cold, and sparingly soluble in boiling *ether,* separating out completely on cooling (Fehling, Müller). — Soluble in *chloroform* (Erdmann), hot *oil of lavender,* and hot *palm-oil* (Heyer).

Anemonic Acid.
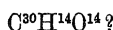
$$C^{30}H^{14}O^{14} ?$$

Literature and *Formation :* see Anemonin (pp. 255, 266). — Not to be confounded with anemoninic acid.

White, tasteless, non-crystalline powder.   Has an acid reaction.

				Fehling.
				mean.
30 C	....	180	58·82	57·87
14 H	....	14	4·57	4·51
14 O	....	112	36·61	37·62
$C^{30}H^{14}O^{14}$	....	306	100·00	100·00

Decomposed by *dry distillation.* Takes fire in a flame and *burns* with incandescence (Heyer), first with a bright flame, then with a glimmering light, and empyreumatic odour, like that of caramel (Schwarz). — *Nitric acid* first turns it yellow, then dissolves it quietly, and deposits flocks on addition of water or hydrochloric acid (Rübenhorst). — It is blackened by *oil of vitriol* (Heyer), and is not sensibly altered by *iodine, chlorine,* or *hydrochloric acid* (Schwartz).

Does not dissolve in *water* or in dilute *acids,* not even in dilute *acetic acid* (Heyer).

It unites with *bases,* forming *salts* (Rabenhorst). It dissolves in *potash-ley,* with yellow colour, turning brown when heated (Heyer). According to Schwarz, it colours *ammonia, potash,* and *soda* yellow, the acid itself assuming an orange-yellow colour; the yellow

liquid is decolorised by hydrochloric acid, with precipitation of yellow flocks ; the orange-yellow powder retains alkali, even after it has been several times washed with water, which renders it paler. — *Baryta* and *lime-water* colour anemonic acid of a paler yellow than the alkalis (Schwarz).

Anemonic acid does not dissolve in *alcohol* or *ether*, *oil of lavender*, or *palm-oil* (Heyer, Fehling).

Primary Nucleus, $C^{30}H^{20}$.

Cedrene.

$C^{30}H^{24}$.

WALTER. *N. Ann. Chim. Phys.* 1, 501 ; *J. pr. Chem.* 24, 232 ; *Ann. Pharm.* 39, 249 ;—*N. Ann. Chim. Phys.* 8, 354 ; *J. pr. Chem.* 30, 367 ; *Ann. Pharm.* 48, 35.

The name *Cedrin* was given by Lewi (*J. Chim. méd.* 1851, 232 ; *Repert.* 109, 350), to neutral bitter needles obtained from the fruit of *Simaba Cedron*, sparingly soluble in cold, easily in boiling water, and in alcohol. The substance may be extracted by alcohol from the fruit after it has been freed from fat by ether.

The volatile oil of *Juniperes virginiana* (*Virginian Cedrene-* or *Juniper-oil*) is a mixture of cedrene and cedar-camphor. It forms a white, soft, crystalline mass. After dehydration, it solidifies at 270°, its temperature then rising to 32° ; on distilling it, the greater part goes over at about 282°, whilst a portion remains altered by the heat.

When oil of cedar, previously distilled and solidified, is subjected to pressure, solid cedar-camphor remains behind, whilst a solution of that substance in cedrene runs off. The latter repeatedly subjected to fractional distillation, yields cedrene boiling between 264° and 268° as the first portion of the distillate. This liquid is purified by repeated distillation over potassium, till the metal is no longer tarnished by it.

When anhydrous phosphoric acid is added by small portions to cedar-camphor $C^{30}H^{20}O^2$, great heat is evolved, and a black viscid oil is obtained, with yellow oil-drops floating upon it. On distilling this product, cedrene passes over, and may be purified by distilling it once or twice over anhydrous phosphoric acid, then repeatedly over potassium.

Properties. Colourless oil, of sp. gr. 0·984 at 14·5°, and boiling at 237°. Has a peculiar aromatic odour, different from that of cedar-camphor ; its taste is at first faintly, afterwards strongly peppery. Vapour-density = 7·9.

							Walter.		
							a.		*b.*
30 C	....	180	....	88·23	....	87·80	....	87·97
24 H	....	24	....	11·77	....	12·01	....	11·95
$C^{30}H^{24}$	....	204	....	100·00	....	99·81	....	99·92

		Vol.		Density.
C-vapour..................		30	....	12·4800
H-gas		24	....	1·6632
Cedrene-vapour		2	... .	14·1432
		1	....	7·0716

a. Cedrene separated from oil of cedar; *b.* prepared from cedar-camphor. Walter gave the formula $C^{32}H^{-6}$; Gerhardt (*Traité* 4, 354), the above.

When cedrene is boiled for a long time, it turns yellow, and its boiling point rises.

Cedar-camphor.

$$C^{30}H^{26}O^2 = C^{30}H^{24},H^2O^2.$$
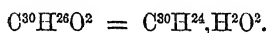
WALTER.   *N. Ann. Chim. Phys.* 1, 498; 8, 354.

Obtained by expressing the crude once-distilled cedar-oil (p. 269), and purified by repeated crystallisation from alcohol.

White, silky needles, which melt at 74°. Boiling point 282°. Has a peculiar aromatic odour, and faint taste. Vapour-density = 8·4.

						Walter.			Vol.	Density.
30 C	180	....	81·08	....	81·0	C-vapour	30	....	12·4800	
26 H	26	....	11·71	....	11·8	H-gas	26	....	1·8018	
2 O	16	....	7·21	....	7 2	O-gas	1	...	1·1093	
$C^{30}H^{26}O^2$	222	....	100·00	....	100·0	Vapour of ce-⎱ dar-camph. ⎰	2 1	....	15·3911 7·6956	

So according to Gerhardt (*Traité* 4, 354); Walter gave the formula $C^{32}H^{28}O^2$.

Decompositions. With *oil of vitriol*, it turns brown, and deposits a yellow oil, without forming a conjugated acid. — *Anhydrous phosphoric acid* converts it into cedrene. — With *pentachloride of phosphorus* it forms an aromatic oil, difficult to obtain pure.

It is nearly insoluble in *water*, but dissolves readily in *alcohol*, either hot or cold.

Cubebene.

$$C^{30}H^{24}.$$

SOUBEIRAN & CAPITAINE.   *J. Pharm.* 26, 73; *Ann. Pharm.* 35, 323.

When cubebs, the fruit of *Piper Cubeba* (*Handbuch* viii., *Phytochem.* 81), is distilled with water, a volatile oil, called *oil* or *essence of cubebs*, passes over, from which, on keeping and cooling, camphor of cubebs separates, while cubebene remains in solution.

If the oil of cubebs is rectified over brine, then dehydrated by leaving it in contact with chloride of calcium for several days, at 40° —45°, and subjected to fractional distillation, water passes over with the oil, being probably formed by decomposition of the camphor of cubebs. The first twelfth part of the distillate, after being again dried by chloride of calcium, is less viscid than the crude oil, has a density of 0·919, and the comparison $C^{30}H^{24}$ (Soubeiran & Capitaine.)

					Soubeiran & Capitaine.
30 C	180	....	88·23	....	87·36
24 H	24	....	11·77	....	11·76
$C^{30}H^{24}$	 204	....	100·00	....	99·12

Camphor of Cubebs.

$$C^{30}H^{36}O^2 = C^{30}H^{24},H^2O^2.$$
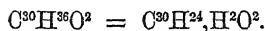
TESCHEMACHER & BROOKE. *Phil. Ann.* 5, 450.
MULLER. *Ann. Pharm.* 2, 90.
SELL & BLANCHET. *Ann. Pharm.* 6, 294.
WINCKLER. *Repert.* 15, 345; *Ann. Pharm.* 8, 203.
AUBERGIER. *J. Pharm.* 27, 278; *Rev. scient.* 4, 220.

Hydrated Oil of Cubebs. Hydrate of Cubebene. See p. 270. — Obtained by cooling oil of cubebs, pressing the solid matter which separates, and recrystallising it from alcohol (Müller); better from ether-alcohol (Blanchet & Sell.)

Colourless, transparent crystals of the right prismatic system, having a vitreous lustre. *Fig.* 66, without the small faces between t and a. Rhombic octahedron a, having its acuter lateral edges truncated by y; the prism u with the end-faces m and t; also a prism u^2 between t and u. $a : a$ in front $= 145° 40'$ (Brooke), $145° 0'$ (Kobell); $a : a$ over $y = 115° 45'$ (Br.); $115° 40'$ (Kob.); $a : a$ over u $= 74° 56'$ (Br.); $75° 24'$ (Kob.); $u : t = 151° 0'$ (Br.); $u^2 : t = 165° 0'$ (Br.). Cleavable parallel to m (Kobell, *Repert.* 45, 351). — Melts between 68·7° and 70° (Winckler), at 69° (Aubergier) to a limpid oil, which solidifies in the crystalline form on cooling. Sp. gr. at the melting point, 0·926 (Aubergier). Boils between 150° and 155° (Winckler), at 150° (Aubergier), and sublimes in small quantities, or distils over without alteration in large quantities (Blanchet & Sell, Müller). — Smells slightly of cubebs; tastes slightly burning at first, afterwards cooling. Neutral.—Lævorotatory; $[a]r = 56·7°$ (Aubergier).

				Blanchet & Sell.		Aubergier.	
				mean.		*mean.*	
30 C	180	....	81·08	......	80·3	....	76·95
26 H	26	....	11·71	....	11·6	....	11·84
2 O	16	... ...	7·21	....	8·1	....	11·21
$C^{30}H^{24},2HO$	222	....	100 00	....	100·0	.... ..	100·00

According to Blanchet & Sell, it is $C^{16}H^{14}O$; according to Aubergier, $C^{30}H^{18}O^2$.

Decompositions. By distillation? (p. 270). — It takes fire when held in a flame, but does not continue to *burn* when removed.'—When triturated with *iodine*, it forms a thick brown liquid. — In *chlorine gas* it melts to a colourless liquid, which, if more chlorine be passed into it, becomes hot and turbid, afterwards clear again, and solidifies to a transparent, tough, yellow-brown, acid mass. — *Oil of vitriol* slowly turns it brown. — *Nitric acid* of sp. gr. 1·5 converts it into a resin, with violent evolution of nitric oxide gas (Winckler).

Immersed in boiling *water*, it melts without dissolving, and distils over slowly with the aqueous vapour (Winckler, Müller). It does not dissolve in *potash-ley*, aqueous *ammonia*, or dilute *acetic acid*. Glacial acetic acid shaken up with camphor of cubebs dissolves it, and the solution, on addition of a larger quantity of the camphor, yields drops of oil, which do not solidify till the acid is neutralised (Müller).

It dissolves readily in *alcohol*, in *ether*, and in *oils*, both *fixed* and *volatile*. According to Blanchet & Sell, it crystallises from the ether-alcoholic, but not from the alcoholic solution.

Hydrochlorate of Cubebene.

$$C^{30}H^{26}Cl^2 = C^{30}H^{24},2HCl.$$
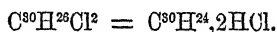
Soubeiran & Capitaine.   *J. Pharm.* 26, 75.

Camphre de Cubèbe.

When hydrochloric acid gas is passed into volatile oil of cubebs, the oil becomes turbid, acquires a dark red-brown colour, and solidifies to a crystalline mass, which may be purified by pressure and recrystallisation from alcohol. The black mother-liquor does not yield any more crystals, even when cooled to − 10°.

Long, oblique prisms, with rectangular base. Sp. gr. 0·801. Boiling point 131°. Lævorotatory; $[\alpha]j = 57\cdot89°$. — Tasteless and scentless.

					Soubeiran & Capitaine.
30 C	180	...	64·9	...	64·3
26 H	26	...	9·3	...	9·3
2 Cl	71	...	25 8	...	24·7
$C^{30}H^{24},2HCl$	277	...	100·0	...	98·3

The vapour passed over red-hot quicklime does not yield any oil, but a small quantity of crystalline sublimate, perhaps naphthalin.

It dissolves in *alcohol* so abundantly, that the solution solidifies on cooling.

Appendix to Cubebene and Camphor of Cubebs.

1. Oil of Cubebs.

For the *Literature* relating to this oil, and for its *constituents*, see page 270.

Cubebs yield 2·1 p. c. of volatile oil (Trommsdorff); 7·8 p. c. (Winckler); 10·7 p. (Steer); 15·6 (Wiking, *N. Br. Arch.* 39; 30).

The oil, after rectification, is colourless and viscid, the last portion which passes over in the fractional distillation having nearly the consistence of butter. Sp. gr. 0·936 at 6·5° (Winckler), 0·929 (Soubeiran & Capitaine); 0·92 (Zeller); 0·92 to 0·936 (Van Hees, *N. Br. Arch.* 61, 18); 0·929 (Williams, *Ann. Pharm.* 107, 242); at 0°, it is 0·924; at 100° it is 0·853 (Aubergier). — The greater portion distils over between 250° and 260°, but leaves a coloured residue, both in this distillation and on subsequent rectification (Soubeiran & Capitaine). Its odour is slightly aromatic, and its taste warming, like that of camphor or peppermint. — Neutral. — Lævoratory; $[\alpha]j$ for the oil dried over chloride of calcium = 40·16; for the same oil, after it has been freed

from the water which forms on distillation (p. 270), it is 39·40° (Soubeiran & Capitaine). Aubergier found for the molecular rotatory power of the portion which distils first $[\alpha]r = 30\cdot98°$; for the last, very viscid portion of the distillate, after separation of the camphor of cubebs which forms at 0°, $[\alpha]r = 28\cdot28°$,—much weaker, therefore, than that of camphor of cubebs, which latter he is disposed to regard as the only optically active constituent of the oil.

Oil of cubebs in contact with *iodine* becomes warm, gives off yellow and violet vapours, and acquires a brown colour and viscid consistence (Winckler). *Nitric acid* does not set the oil on fire, but heats it strongly, and converts it into a resin, with copious evolution of nitrous vapours. — When dropt into a large quantity of *oil of vitriol*, it forms a red-brown solution, containing a conjugated sulpho-acid (Gerhardt, *Compt. rend.* 17, 314). Heated with oil of vitriol, it makes a loud and continued hissing noise, and gives off a colourless oil, which, after precipitation, exhibits a slight lævoratory power ($[\alpha]r = 5\cdot25$), and is perhaps identical with cubebene (Aubergier.) — *With bichromate of potash* and oil of vitriol, oil of cubebs assume a greenish colour (Zeller). With absolute *acohol*, it forms a turbid mixture ; with 27 pts. alcohol of sp. gr., 0·87, an opalescent mixture (Zeller).

2. Cubebin.

MONHEIM. *Repert.* 44, 199.
CASSOLA. *J. Chim. méd* 10, 68 ; abstr. *Repert.* 50, 220 ; *N. Br. Arch.* 3, 303.
STEER. *Repert.* 61, 85 ; *N. Br. Arch.* 12, 197. — *Repert.* 71, 119 ; *N. Br. Arch.* 24, 207.
SOUBEIRAN & CAPITAINE. *J. Pharm.* 25, 355 ; abstr. *Repert.* 67, 113 ; *N. Br. Arch.* 19, 173 ; *Ann. Pharm.* 31, 190 ; *J. pr. Chem.* 17, 480.
SCHUCK. *N. Repert.* 1, 213.
ENGELHARDT. *N. Repert.* 3, 1.

Discovered by Monheim ; prepared pure by Soubeiran & Capitaine.

Occurrence. In cubebs, the not perfectly ripe fruit of *Piper Cubeba* (*Handbuch* viii., *Phytochem.* 81). Separates from the ethereal extract of cubebs on keeping (Schuck, Engelhardt).

Preparation. From cubebs, freed from volatile oil by distillation with water, then pressed and dried. The cubebs are exhausted with boiling alcohol, the decoctions are evaporated to an extract ; this extract is treated with caustic potash, to remove certain substances soluble therein ; and the cubebin which remains is washed with water and purified by repeated recrystallisation from alcohol (Soubeiran & Capitaine). From the alcoholic tinctures, after sufficient concentration, the cubebin crystallises on cooling, and may be purified by recrystallisation, with help of animal charcoal (Steer).

Schuck employs cubebs not previously freed from volatile oil, adding $\frac{1}{8}$ of their weight of quick lime. — Monheim exhausts the cubebs with ether, before treating them with alcohol, in which process, however, the

ether, by help of the volatile oil, dissolves a portion of the cubebin (Engelhardt). — The ethereal extract of cubebs prepared in the percolator, yields, by spontaneous, evaporation needle-shaped crystals mixed with oil and resin ; they may be obtained pure by washing with potash-ley and recrystallisation from alcohol, or from boiling acetic acid (Riegel, *N. Jahrb. Pharm.* 8, 96).

The product (varying perhaps in quantity according to the age of the cubebs) amounts to 5·35 p. c. of crude cubebin (Steer), 0·18 p. c. (Schuck).

Properties. Small, white needles (Soubeiran and Capitaine) ; laminæ having a silky or pearly lustre. Does not lose weight in vacuo at 200°, and may be fused without decomposition (Soubeiran & Capitaine). Melts at 120°, and solidifies to a tough greenish-yellow resin on cooling (Schuck). Inodorous, tasteless, and neutral.

	a			b			Soubeiran. & Capitaine.
20 C	120	....	67·41	34 C	204	....	68·00	....	66·91
10 H	10	....	5·62	16 H	16	....	5·33	....	5·68
6 O	48	....	26·97	10 O	80	....	26·67	...	27·41
$C^{26}H^{10}O^6$	178	....	100·00	$C^{34}H^{16}O^{10}$	300	....	100·00	....	100·00

Soubeiran & Capitaine's analyses, when recalculated, agree better with the formula *a*, than with their own formula $C^{34}H^{17}O^{10}$ (Kr.).

Decompositions. Cubebin when *heated*, swells up, gives off white fumes, and burns with a bright flame, leaving a considerable quantity of charcoal. — Hot nitric acid colours it dark reddish yellow, and gives off nitrous gas (Schuck). — With *oil of vitriol* it assumes a fine blood-red colour, the mixture becoming carbonised when heated (Soubeiran & Capitaine, Schuck). — It is not altered by hot *hydrochloric acid* (Schuck).

It is nearly insoluble in cold, and but slightly soluble in hot *water*. — It is not altered by *alkalis* and *earths*, and does not unite with them, — It dissolves in *acetic acid*, especially when hot, and crystallises on cooling.

It dissolves at 20°, in 76 pts. absolute *alcohol*, and in 140 pts. alcohol of sp. gr. 0·85 (Soubeiran & Capitaine) ; in 200 pts. cold and 10 pts. boiling alcohol (Schuck). It dissolves in 26·6 pts. *ether* of 12° (Soubeiran & Capitaine), sparingly in *chloroform*, more readily in *oils* both *fixed* and *volatile*.

Lactucerin.

$$? \ C^{30}H^{24}O^2 = C^{30}H^{24},O^2.$$
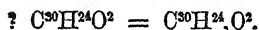
Walz. *Ann. Pharm.* 32, 85 ; *Pharm. Centr.* 1840, 59 ; *Jahrb. pr. Pharm.* 14, 25.

Lenoir. *Ann. Pharm.* 60, 83.

Ludwig, Thieme, & Ruickholdt. *N. Br. Arch.* 50, 1, and 129.

Walz's *Lettuce-fat* ; Lenoir's *Lactucone* ; Ludwig's *Lactucerin.* — Occurs in

lactucarium, the milky juice of *Lactuca virosa (Handbuch* viii. *Phytochem-* 69). On other bodies prepared from lactucarium, see page 278, and *Handbuch.* viii. 69.

Preparation. Chopped lactucarium is" repeatedly exhausted with boiling alcohol, and the tinctures are filtered while hot. The liquid, on cooling, deposits nodules of lactucerin, contaminated with colouring matter and bitter principle, from which they may be purified by repeated crystallisation from alcohol, with help of animal charcoal (Lenois).

Ludwig treats the lactucarium with water, before exhausting it with alcohol, and frees the lactucerin from admixed bitter principle by washing with water. — The fresh milky juice of *Lactuca virosa* deposits, when mixed with water, a white curdy mass, from which alcohol extracts lactucerin. — Dry lactucarium yields as much as 53 p. c. lactucerin.

Properties. Slender, colourless needles, united in stellate groups, melting between 150° and 200° to an amorphous mass, and solidifying to an amorphous transparent mass on cooling. In a stream of carbonic acid it volatilises for the most part undecomposed. Scentless, tasteless, neutral, and without action on the animal organism (Lenoir).

			Lenoir. mean.		Ludwig.
30 C	180	....	81·81	.... 81·00	.... 81·08
24 H	24	....	10·91	.... 11·11	... . 11·41
2 O	16	......	7·28	.... 7·89	.... 7·51
$C^{30}H^{24}O^{2}$	220	....	100·00	.... 100·00	.... 100·00

In other analyses, Ludwig & Ruickholt found from 1 to 5 p. c. less carbon, doubtless in consequence of impurity of the lactucerin.

Decompositions. When heated, it partly creeps, undecomposed, up the sides of the vessel, and partly decomposes, yielding a large quantity of acetic acid (Lenoir). When subjected to dry distillation, it first gives off white fumes which condense to a colourless acid liquid, then heavy, yellow vapours, and a dark-coloured oil, while a small quantity of charcoal remains. No carbonic acid or combustible gas is evolved in the decomposition (Ludwig). — Lactucerin dissolves in *oil of vitriol*, forming a brown solution which chars when heated (Ludwig). — It is not altered by *chlorine gas* (Lenoir). Heated with *nitric acid* of sp. gr. 1·25, it dissolves, and leaves on evaporation a yellow residue, which is soluble in aqueous ammonia, and is precipitated from the solution by acetic acid (Ludwig).

Lactucerin is insoluble in *water*. It is not altered by aqueous or alcoholic *potash*, and is not precipitated from its alcoholic solution by *metallic salts* (Lenoir).

It is soluble in *alcohol*, in *ether*, and in *oils* both *fixed* and *volatile* (Lenoir).

Appendix to Lactucerin.

Lactucin.

WALZ.   *Ann. Pharm.* 32, 85. — *Jahrb. pr. Pharm.* 14, 25. — *N. Jahrb. Pharm.* 15, 118.
AUBERGIER.   *Compt. rend.* 19, 923 ; *Ann. Pharm.* 44, 299.
LUDWIG.   *N. Br. Arch.* 50, 1, and 129.
KROMAYER.   *N. Br. Arch.* 105, 3.
LUDWIG & KROMAYER.   *N. Br. Arch.* 111, 1.

The bitter principle of Lactucarium.   Occurs in the milky juice of *Lactuca altissima* (Aubergier). — From the alcoholic extract of *Lactuca sativa* Pagenstecher (*Ann. Pharm.* 10, 323 : *Pharm. Centr.* 1841. 14) extracted with alcohol of 95 p. c. white, bitter crystals, having the consistence of wax, incapable of uniting with acids or with alkalis, soluble in all proportions in water and alcohol, insoluble in ether.   It is doubtful whether these crystals consisted of lactucin.

Preparation.   Fresh German lactucarium is drenched with 1½ pts. of hot water, and pressed after standing for fourteen days ; and the residue is stirred up with cold water to a pulp and again pressed, whereby oxalic acid and other substances are dissolved, and a residue is obtained consisting chiefly of lactucin and lactucerin.   This residue is boiled at least five times with fresh quantities of water, as long as the extracts acquire a bitter taste, whereupon lactucin dissolves while lactucerin remains undissolved.   The united aqueous extracts, evaporated till they amount to half the weight of the lactucarium employed, solidify on cooling to a granular mass, which must be separated from the mother-liquor, dissolved in hot water, and mixed with basic acetate of lead.   The precipitate is washed with hot water ; hydrosulphuric acid gas is passed into the filtrate ; and the liquid is again filtered, evaporated, and left to itself.   Lactucin then crystallises out after a while, and a further quantity is obtained on concentrating the mother-liquor. It may be purified by recrystallisation from hot alcohol, with help of animal charcoal. — The mother-liquors of the granular mass, when freed from substances precipitable by basic acetate of lead, then from excess of lead, and evaporated, yield an additional quantity of lactucin, till at length nothing remains but uncrystallisable lactucopicrin (Ludwig & Kromayer).   The yield is about $\frac{3}{10}$ p. c. of the lactucarium, or less (Kromayer). — Walz exhausts pulverised lactucarium with a warm mixture of alcohol and $\frac{1}{50}$ concentrated acetic acid ; adds a large quantity of water, then basic acetate of lead, as long as a precipitate is thereby produced ; and washes this precipitate with weak alcohol containing acetic acid.   The filtrate, freed from lead by hydrosulphuric acid, is evaporated to dryness at about 60°, and the residue is exhausted with ether, from which, on evaporation, the lactucin crystallises.   It is purified by solution in weak alcohol, evaporation, and resolution in ether. — Or he exhausts the above residue with absolute alcohol, evaporates and treats with ether, which takes up the lactucin.
Ludwig, by the following process, obtained lactucin, together with his *lactucic acid* :
80 grammes of finely pulverised lactucarium are triturated with an equal quantity of dilute sulphuric acid containing $\frac{1}{6}$ oil of vitriol ;

400 gr. alcohol of 84 p. c. is added; the liquid is shaken and filtered; the reddish-yellow filtrate agitated with crumbled hydrate of lime till a filtered sample is not rendered turbid, either by baryta-water or by oxalate of potash; the filtrate decolorised by animal charcoal; the greater part of the alcohol distilled off; and the remaining liquid evaporated. It then deposits a brown viscid mass, which may be washed with cold water and heated to boiling with a large quantity of water. The lactucerin, which then separates in the form of resin, is removed, and the aqueous solution is decolorised with animal charcoal and evaporated, whereupon a mixture of lactucin and lactucic acid crystallises out, to be separated by boiling water, from which the former crystallises in scales. On evaporating the mother-liquors, lactucic acid remains, as an amorphous light-yellow mass, which crystallises after long standing.

Properties. Lactucin forms white scales having a pearly lustre, like crystallised boracic acid; melting to a colourless mass when heated (Aubergier, Ludwig). From very dilute alcohol it crystallises in rhombic tables (Kromayer). Its taste is strongly and purely bitter. Neutral.

							Kromayer.
22	C	132		65 67			65·22
13	H	13		6 47			6 68
7	O	56		27 86			28·10
$C^{22}H^{12}O^6,HO$		201		100·00			100·00

							Kromayer.
22	C	132		62·86			62·62
14	H	14		6·66			6·80
8	O	64		30·48			30·58
$C^{22}H^{12}O^6,2HO$		210		100·00			100·00

So, according to Kromayer.

Lactucin chars when *heated*, without subliming (Aubergier). — With *oil of vitriol* it turns brown (Walz); dissolves in cold oil of vitriol, and blackens that liquid when heated with it (Ludwig). The colourless solution, if cautiously heated, assumes a fine cherry-red colour (Kromayer). — It is not altered by cold strong *hydrochloric acid*, but dissolves in it when hot, the solution assuming a red colour, and depositing resin when boiled (Kromayer). — It is not altered by *nitric acid* of sp. gr. 1·2, but is resinised by nitric acid of sp. gr. 1·48 (Walz). Strong nitric acid dissolves it without coloration (Kromayer). *Caustic alkalis* and *lime-water* colour aqueous lactucin wine-red, the colour changing to brown when the liquid is heated (Kromayer). — Lactucin treated with alkalis loses its bitterness, which is not restored by acids (Aubergier). — From an *alkaline cupric solution* it throws down cuprous oxide, and from *nitrate of silver* mixed with caustic soda (not from an acid or ammoniacal silver-solution) it separates metallic silver (Ludwig).

Lactucin is not altered by *iodine-water*, by *ferric acetate* or *hydrochlorate*, or by *acetate of lead*, either neutral or mixed with ammonia (Ludwig). It is not a conjugated sugar-compound.

Lactucin dissolves in from 60 to 80 pts. cold, and in a smaller quantity of boiling *water* (Walz). It is nearly insoluble in cold water,

less soluble in boiling water than in *alcohol,* and insoluble in *ether* (Aubergier, Kromayer). It dissolves readily in *acetic acid* (Walz).

Lactucic acid. Preparation (p. 277). Has a strong and persistently bitter, not sour taste, and reddens litmus. The aqueous solution is reddened by alkalis. It reduces alkaline cupric solution and ammoniacal silver-solution at the boiling heat, throws down from neutral acetate of lead, a white precipitate soluble in excess of the lead-salt, and from ferric acetate a white precipitate soluble in acetic acid (Ludwig).

Lactucopicrin. Preparation (p. 277). — The lactucopicrin remaining in the mother-liquors is freed from admixed lactucin and lactucerin by ether. — Brown, amorphous, very bitter mass, having a very faint acid reaction. Soluble in water and alcohol, and not precipitated by basic acetate or lead. Contains 56·62 p. c. C., 6·83 H., and 36·35 O., corresponding to the formula C⁴⁴H³²O²¹, and is therefore produced from lactucin by assumption of water and oxygen (Kromayer, *Die Bitterstoffe,* Erlangen, 1861, 79).

Primary Nucleus C³⁰H²⁶; *Oxygen-nucleus* C³⁰H¹²O¹⁴.

Fraxetin.

$$C^{30}H^{12}O^{16} = C^{30}H^{12}O^{14},O^2.$$
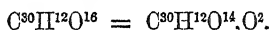
SALM-HORSTMAR. *Pogg.* 100, 607; *N. Repert.* 6, 359.—*Pogg.* 107, 327; *J. pr. Chem.* 78, 365.
ROCHLEDER. *Wien. Akad. Ber.* 40, 37; *Chem. Centr.* 1860, 481; *N. Repert.* 9, 400; *J. pr. Chem.* 80, 173.

Obtained from fraxin by boiling with dilute acids, perhaps also by dry distillation. Salm-Horstmar heats 1 pt. by weight of fraxin with 4 pts. by measure of dilute sulphuric acid containing half its volume of oil of vitriol, whereupon fraxetin separates from the solution after a few minutes.

Properties. The yellowish crystals of hydrated fraxetin (see below) are converted, between 100° and 120°, into white anhydrous fraxetin (Rochleder). — It melts at about 230°, without turning brown, and solidifies in the crystalline form. — Its taste is very slightly astringent, Inodorous. The concentrated hot aqueous solution has an acid reaction (Salm-Horstmar).

	at 120°.			Rochleder.
30 C	180	56·25		56·18
12 H	12	3·75		3·63
16 O	128	40·00		40·19
C³⁰H¹²O¹⁵	320	100·00		100·00

Combinations. — *With Water.* — *Hydrated Fraxetin.* — Colourless (yellowish, according to Rochleder) transparent needles, and fern-like laminæ. From solution in alcohol it separates on cooling in microscopic

rectangular, rhombic, and six-sided tables; by spontaneous evaporation, in larger tables probably belonging to the right prismatic system (Salm-Horstmar). — Below 100° it gives off 4·36 p. c. water (1½ at. = 4·05 p. c. HO) (Rochleder).

Fraxetin dissolves in 10,000 pts. of cold, and in 33 pts. of boiling *water*. — It dissolves in *oil of vitriol*, with bright yellow colour, and may be precipitated from the solution, after dilution with water, by ammonia. It dissolves with yellow colour in warm *hydrochloric acid*, and crystallises out on cooling; with *nitric acid* it forms a dark violet solution, changing through garnet- and rose-red to yellow, and ultimately becoming colourless (Salm-Horstmar).

Its aqueous solution is coloured yellow to orange by *ammonia*, also by alkaline carbonates, and yields a brown precipitate. The solution of fraxetin in aqueous *sulphite of ammonia* is turned yellow by ammonia. — The hydrates of the alkaline earths immersed in a solution of fraxetin become covered with a red deposit, which, with *baryta* and strontia, becomes black-green, with *lime* and *magnesia* brownish. The *carbonates of the alkaline earths* colour the solution of fraxetin yellow, and then throw down a precipitate, exhibiting a green fluorescence, and insoluble in water. — Fraxetin colours *acetate of baryta* and *acetate of strontia* yellow, changing to green on evaporation; from *acetate of cadmium* and *acetate of lead*, it throws down lemon-yellow precipitates. Its solution, mixed with a very small quantity of *ferric hydrochlorate*, assumes a dark greenish blue colour; with *acetate of silver* it forms a black precipitate, differing in appearance from metallic silver (Salm-Horstmar).

Fraxetin dissolves in *alcohol* much more abundantly than in water, and is slightly soluble in warm *ether* (Salm-Horstmar).

Glucoside of Fraxetin.

Fraxin.

$$C^{54}H^{30}O^{34} = C^{30}H^{10}O^{14}, 2C^{12}H^{10}O^{10}.$$
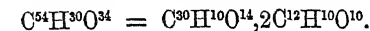
SALM-HORSTMAR. *Pogg.* 97, 637; further *Pogg.* 100, 607; *N. Repert.* 6, 359; abstr. *J. pr. Chem.* 71, 250; *Chem. Centr.* 1857, 452.—*Pogg.* 107, 327; *J. pr. Chem.* 78, 365; *N. Repert.* 9, 396.

STOKES. *Chem. Soc. Qu. J.* 11, 17; *J. pr. Chem.* 79, 115; *N. Repert.* 9, 398. — *Chem. Soc. Qu. J.* 12, 126; abstr. *Kopp's Jahresb.* 1859, 578.

ROCHLEDER. *Pogg.* 107, 331; *J. pr. Chem.* 78, 366.—*Wien. Akad. Ber.* 40, 37; *Chem. Centr.* 1860, 481; *N. Repert.* 9, 400.

Paviin.—L. Gmelin (*Ann. Pharm.* 34, 354) some years ago observed the fluorescent property of manna obtained from a species of *Fraxinus*, but attributed the property to æsculin.—Fraxin was discovered by Salm-Horstmar.—Keller's *Fraxinin* (*Repert.* 44, 338), obtained from *Fraxinus excelsior* in the same manner as salicin from willow-bark, was shown by Rochleder & Schwarz (*Wien. Akad. Ber.* 10, 76) and by Stenhouse (*Ann. Pharm.* 91, 295) to be nothing but mannite. — On Mouchon's *Fraxinite*, the purgative principle of ash-leaves, see *Pharm. Viertelj.* 3, 433. It is uncrystallisable, and was not obtained pure.

Occurrence. In the bark of *Fraxinus excelsior* (Salm-Horstmar), of

Aesculus Pavia and *Aes. Hippocastanum*, as well as in the bark of allied species of the same genera (Salm-Horstmar).

Preparation. A. *From Horse-chesnut bark.* — 1. The bark is exhausted with alcohol of 35° B.; the filtrate is precipitated with an alcoholic solution of neutral acetate of lead; and the precipitate is washed with alcohol and decomposed under water by hydro-sulphuric acid. The liquid filtered from the sulphide of lead, is evaporated to dryness in vacuo over sulphuric acid; the residue is triturated with a small quantity of water at 0°; the solution of tannic acid thereby obtained is removed by rapid filtration; and the crystals which remain are washed with ice-cold water, and dried in a vacuum, at a temperature below 100° (Rochleder).

2. The cooled decoction of horse-chesnut bark is mixed with the aqueous solution of a ferric salt, which is added by separate portions, till the flocks produced in a sample of the liquid on addition of ammonia settle rapidly down, leaving the supernatant liquid of a pure yellow colour, and strongly fluorescent. The whole is then precipitated by ammonia, and the liquid filtered; one-fourth of the filtrate is mixed with a quantity of neutral acetate of lead sufficient to precipitate the whole of it, then with sufficient acetic or nitric acid to re-dissolve the precipitate; the remaining three-fourths of the filtrate are likewise acidulated; and the two liquids are mixed. From the acid solution thus prepared, containing acetate of lead, ammonia throws down a precipitate containing fraxin, from which the fraxin may be obtained in the crystallised state, by dissolving it out with acetic acid, and leaving the filtrate at rest (Stokes). The filtrate freed from the lead-compound of fraxin still contains æsculin (p. 19) which may be precipitated by basic acetate of lead, and separated from this precipitate in the same manner as fraxin from its lead-compound (Stokes).

B. *From the bark of the Ash-tree (Fraxinus excelsior).* — The decoction of the bark collected in spring when the tree is in flower, and dried, is precipitated with neutral acetate of lead; the liquid filtered therefrom is precipitated by basic acetate of lead; and the latter precipitate is pressed and decomposed under water by hydrosulphuric acid. The sulphide of lead is removed; the filtrate evaporated to a syrup over the water-bath; and the crystals which separate after 24 hours, are collected, washed with water, as long as the liquid which runs off exhibits a whitish turbidity, then with a small quantity of alcohol, and purified by recrystallisation (Salm-Horstmar).

Properties. Hydrated fraxin forms tufts of needles, consisting of slender four-sided prisms, having a dazzling white colour, with a tinge of sulphur-yellow (Salm-Horstmar). From a hot saturated solution in absolute alcohol, it separates on cooling in colourless crystals, resembling those of sulphate of zinc, and not turning yellow when dry (Rochleder). Inodorous. Has a slightly bitter and astringent taste. In a very dilute aqueous or alcoholic solution, especially if it contains a trace of ammonia or fixed alkali, it exhibits by daylight a blue or bluish-green fluorescence, which disappears on addition of acids (Salm-Horstmar, Stokes).

Crystallised fraxin dried in vacuo at temperatures below 110°, still

retains 1 at. water; that which has been dried between 110° and 113° contains no water (Rochleder).

	Below 110°.			Kawalier. *mean.*
54 C	324	....	51·02	.... 51·12
31 H	31	....	4·88	.... 5·07
35 O	280	....	44·10	.... 43·81
$C^{54}H^{30}O^{34},HO$	635	....	100·00	.... 100·00

	Between 110° *and* 113°.			Rochleder. *mean.*
54 C	324	....	51·66	.... 51·61
30 H	30	....	4·79	.... 4·79
34 O	272	....	43·55	.... 43·60
$C^{54}H^{30}O^{34}$	626	... .	100·00	.... 100·00

This formula alone—not the formula $C^{42}H^{23}O^{27}$ formerly proposed by Rochleder [or $C^{12}H^{22}O^{26}$ by Wurtz (*Rép. Chim. pure* 1, 473)]—agrees with the quantities of sugar obtained by the decomposition of fraxin.

Decompositions. 1. Fraxin *heated* to 320°, gives off water, and melts to a red liquid, which solidifies on cooling, to an amorphous fissured mass, crumbling to a cream-coloured powder, probably fraxetin, when water is poured upon it, and dissolving with yellowish red colour in alkaline water (Rochleder). On applying a stronger heat, it gives off an odour of burnt sugar, together with white fumes which condense to crystalline drops, very soluble in water, and becoming yellow and fluorescent when treated with aqueous ammonia. If the heat be continued till nothing but charcoal remains a brownish yellow deposit is produced, which, when moistened with water, yields crystals, insoluble in water, but soluble in alcohol (Salm-Horstmar).— 2. Fraxin dissolved in water, is resolved by boiling with dilute acids into fraxetin and crystallisable sugar, of which substance fraxin not quite pure (? hydrated) yields 54 p. c. (Rochleder).

$$C^{54}H^{30}O^{34} + 6HO = C^{30}H^{12}O^{16} + 2C^{12}H^{12}O^{12}.$$
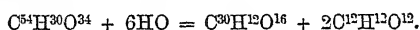
The calculated quantity for anhydrous fraxin is 57·2 p. c. ; for hydrated, 56·7 p. c.

Combinations. Fraxin dissolves in 1,000 pts. water at 14°, easily in hot water. — It is coloured sulphur-yellow by *oil of vitriol*, also in aqueous solution by *ammonia*, and by the *fixed alkalis* or *alkaline carbonates ;* the crystals are also coloured yellow by ammonia gas (Salm-Horstmar). In aqueous solution it colours *neutral* or *basic acetate of lead* yellow, without precipitation. With an ammoniacal solution of neutral acetate of lead, it forms a yellow precipitate ; and by digestion with hydrated lead-oxide, yellow crystalline spherules. — It does not precipitate *ferrous sulphate*, but when added to solution of *ferric chloride*, it first colours the liquid green, and then forms a lemon-yellow precipitate. — It does not produce any turbidity in solution of *cupric acetate*, *tartar-emetic*, or *gelatin* (Salm-Horstmar).

It dissolves sparingly in cold, easily in hot *alcohol*, but is insoluble in *ether* (Salm-Horstmar). According to Stokes, on the other hand, it is more soluble in ether than æsculin, forming a fluorescent solution, from which it may be extracted by water. — It is precipitated on *animal charcoal* immersed in its aqueous solution (Salm-Horstmar).

Azo-nucleus $C^{30}N^2H^{24}$.

Sparteine.

$$C^{20}N^2H^{26} = C^{30}N^2H^{24}, H^2.$$
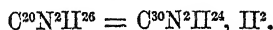
E. J. MILLS. *Chem. Soc. J.* 15, 1; *Ann. Pharm.* 125, 71; *Chem. Centr.* 1862, 700.

Vid. xiii, 152. — Mills confirms the formula given by Stenhouse, which, however, he doubles; spartcine would, therefore, be properly described in this place, and not in vol. xiii. We may here notice the recent investigations respecting it (Kr).

Preparations. The plant is exhausted with water containing sulphuric acid; the solution is concentrated; the residue distilled with soda-ley; the distillate evaporated to dryness, after being acidulated with hydrochloric acid; the residue mixed with pulverised hydrate of potash; and the slightly moistened mixture distilled, whereupon ammonia escapes and spartein passes over as an oil. It is dehydrated by prolonged heating with sodium in a current of hydrogen (which is the only way of dehydrating it completely), and rectified *per se* — 100 lbs. *spartium* yield 22 cub. cent. spartein.

It contains (as found by Stenhouse, xiii., 152), 76·86 p. c. C., and 11·45 H., agreeing with the formula $C^{30}N^2H^{2}$ (calc. xiii. 152).

From its behaviour to iodide of ethyl, with which it forms ethyl- and biethyl-sparteine, it appears to be a tertiary diamine $(C^{30}H^{26})^{vi}N^2$, *i.e.*, a compound corresponding to 2 at. ammonia in which the group of atoms $C^{30}H^{26}$ plays the part of 6 at. hydrogen, and convertible, by assumption of 1 at. C^4H^4 and 4 at. water, or of 2 at. C^4H^4 and 4 at. water, into compounds, each of which corresponds to 2 at. hydrated oxide of ammonium.

Sparteine forms amorphous resinous salts with *hydriodic, hydrobromic,* and *hydrochloric acids.*

Iodozincate of Sparteine $C^{30}N^2H^{26},2HI,2ZnI$ is obtained on mixing the solutions of hydriodate of spartein and iodide of zinc, in slender needles, which quickly turn brown when exposed to the air. Contains 62·39 p. c. iodine (calc. 62·78 p. c. I).

Chlorozincate of Sparteine. Beautiful white needles, sometimes half an inch long, moderately hard and lustrous.

Chloroaurate of Sparteine (xiii. 153). Contains 32·18 p. c. gold, the formula $C^{30}N^2H^{26},2HCl,AuCl^3$, requiring 32·27 p. c. Au.

The *platinum-salt* has the composition given at xiii. 154, I. — The *oxalate* crystallises in needles.

Ethyl-sparteine.

$$C^{34}N^2H^{30} = C^{30}N^2H^{23}(C^4H^5), H^2.$$

MILLS. *Ann. Pharm.* 125, 74.

Vinespartein (see above).

When a mixture of equal volumes of sparteine, iodide of ethyl, and alcohol is heated to 100° for an hour, a dark-coloured liquid is formed,

which deposits crystals. These, when purified by washing with cold, and recrystallisation from warm alcohol, consist of hydriodate of ethyl-sparteine. Their aqueous solution is decomposed by oxide of silver, yielding a strongly alkaline solution of *hydrated ethyl-sparteine*.

This alkaline solution heated to 100° with *iodide of ethyl* and alcohol, yields biethyl-sparteine, which remains mixed with iodine, on evaporating the liquid.

Hydriodate of Ethyl-sparteine crystallises in long radiating needles. It is not decomposed by boiling potash-ley.

			Mills. mean.
34 C	204	39·38	39·30
2 N	28	5·40	
32 H	32	6 18	6·43
2 I	254	49·04	49·02
$C^{30}N^2H^{25}(C^4H^5),2HI$	518	100 00	

Hydriodate of ethyl-sparteine is decomposed by *chloride of silver*, with formation of hydrochlorate of ethyl-sparteine, which crystallises in needles, and forms a crystallisable double salt with *chloride of zinc.* — Hydrochlorate of ethyl-sparteine, mixed in the cold with *bichloride of platinum*, forms *chloroplatinate of ethyl-sparteine*, as a semi-crystalline precipitate, soluble in water, alcohol, and especially in hydrochloric acid.

	Over oil of vitriol.		Mills.
$C^{34}N^2H^{32}Cl^6$	477·0	70·74	
2Pt	197·4	29·26	29·17
$C^{30}N^2H^{25}(C^4H^5),2HCl,2PtCl^2$	674·4	100·00	

Biethylsparteine.

$$C^{38}N^2H^{34} = C^{30}N^2H^{22}(C^4H^5)^2,H^2.$$
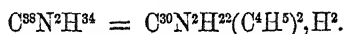
MILLS. *Ann. Pharm.* 125, 76.

When an aqueous solution of ethyl-sparteine is heated for some time to 100° in a sealed tube, with alcohol and iodide of ethyl, and the contents of the tube are subsequently evaporated in a stream of hydro-sulphuric acid gas, *hydriodate of biethylsparteine* remains, and may be obtained in short crystals by crystallisation from alcohol. From this compound, in the manner already described for ethyl-sparteine, may be obtained *aqueous biethylsparteine*, and the *hydrochlorate* and *chloroplatinate of biethylsparteine*. The last-mentioned salt is pale yellow, separates from weak alcohol in radiating crystals, is easily soluble in water, and is only partially precipitated by ether-alcohol. It contains 28·64 p. c. platinum, agreeing approximately with the formula $C^{30}N^2H^{24}(C^4H^5)^2,2HCl,PtCl^2$ (calc. 28·1 p. c. Pt).

Primary-nucleus $C^{30}H^{28}$.

Cimicic Acid.

$$C^{30}H^{28}O^4 = C^{30}H^{28},O^4.$$
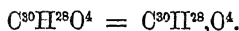
CARIUS. *Ann. Pharm.* 111, 147; abstr. *J. pr. Chem.* 81, 398; *Zeitschr. Ch. Pharm.* 3, 185; *Chem. Centr.* 1860, 567.

Occurrence. In the grey leaf-bug, *Rhaphigaster punctipennis*, chiefly in a cavity of the abdomen from which the animals eject an offensive liquid.

Preparation. The insects killed by immersion in strong alcohol, lose their odour when left for several days in an open vessel half filled with alcohol, and yield to that liquid a brown resin. The adhering alcohol is left to evaporate; the insects are crushed in a mortar, and exhausted with ether; and the ethereal solution is evaporated. From the remaining brown oil, which solidifies in the cold, a baryta-salt is prepared, which, when washed with water and dilute alcohol, and decomposed by hydrochloric acid, yields cimicic acid. The product thus obtained is washed with warm water, dried by chloride of calcium, and lastly filtered and crystallised from ether.

Properties. Colourless needles, arranged in stellate groups, melting at 43·8—44·2°, and exhibiting the same temperature when solidified. Lighter than water. — Has a very faint rancid odour. The alcoholic solution has an acid reaction.

		Dried over the water-bath.		Carius. mean.
30 C	180	....	75·00	74·91
28 H	28	....	11·67	11·74
4 O	32	....	13·33	13·35
$C^{30}H^{28}O^4$	240	....	100·00	100·00

Belongs to the oleic series. Not decomposible by Heintz's method of fractional precipitation (xv. 45).

Decompositions. By *dry distillation* it yields a large quantity of gas, and an oil which solidifies on cooling, and appears to contain a portion of the unaltered acid. With *pentachloride of phosphorus* it forms chloride of cimicyl. By fusing it with *hydrate of potash*, and distilling the product with sulphuric acid, a distillate is obtained containing acetic acid, and a residue from which drops of oil separate.

Insoluble in *water.*

The *cimicates* have the composition $C^{30}H^{27}MO^4$. The solutions of the alkaline salts froth like soap-water, and are precipitated by concentrated solutions of hydrate of potash, hydrate of soda, or common salt. The alkaline cimicates form clear solutions with a small quantity of water, but are rendered turbid by a large quantity. The other salts are insoluble in water and in alcohol, and with the exception of the lead-salt, likewise insoluble in ether.

Cimicate of Potash. — A solution of cimicic acid in absolute alcohol

is mixed with a slight excess of hydrate of potash, and carbonic acid is passed into the solution, till the alkaline reaction disappears, after which the liquid is filtered and evaporated. — Amorphous hygroscopic mass. Melts when heated.

				Carius.
$C^{30}H^{27}O^4$	239·0	85·91		
K	39·2	14·09		14·39
$C^{30}H^{27}KO^4$	278·2	100·00		

Cimicate of Soda. — From a solution of the acid in dilute soda-ley, this salt is precipitated, on addition of strong soda-ley, in granular masses, which may be purified by pressure and solution in absolute alcohol. The filtrate, on cooling, deposits the greater part of the salt in thick flakes, the rest, on further cooling, as a granular jelly. — The salt, when dry, forms a white soap. It is permanent in the air.

	at 100°.			Carius.
$C^{30}H^{27}O^4$	239	91·22		
Na	23	8·78		8·54
$C^{30}H^{27}NaO^4$	262	100·00		

Cimicate of Baryta. Precipitated from the solution of the soda-salt in dilute alcohol, by chloride of barium, in white curdy flakes, which are somewhat soluble in hot water, and bake together in drying.

				Carius. *mean.*
$C^{30}H^{27}O^4$	239·0	77·73		
Ba	68·6	22·27		22·06
$C^{30}H^{27}BaO^4$	307·6	100·00		

Cimicate of Lime. — Obtained like the baryta-salt, which it resembles.

				Carius. *mean.*
$C^{30}H^{27}O^4$	239	92·28		
Ca	20	7·72		7·58
$C^{30}H^{27}CaO^4$	259	100·00		

Cimicate of Lead. — White flocks, which dry up to a yellowish mass, not fusible without decomposition. Somewhat soluble in ether.

				Carius. *mean.*
$C^{30}H^{27}O^4$	239	69·75		
Pb	104	30·25		29·47
$C^{30}H^{27}PbO^4$	343	100·00		

Cimicate of Silver. White flocks, friable when dry. Becomes dark-coloured on exposure to light, and black at a temperature below 100°.

				Carius.
$C^{30}H^{27}O^4$	239	68·88		
Ag	108	31·12		31·43
$C^{30}H^{27}AgO^4$	347	100·00		

Cimicic acid dissolves with difficulty in absolute *alcohol*, in all proportions in *ether*, crystallising from the latter as it cools.

Cimicate of Ethyl.

$$C^{34}H^{32}O^4 = C^4H^5O,C^{30}H^{27}O^3.$$
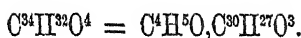
Carius. *Ann. Pharm.* 144, 154.

Cimicic ether. Cimicylvinester. — Obtained by heating chloride of cimicyl with alcohol for a considerable time, precipitating the solution with water, and drying over chloride of calcium.

Light yellow oil, solidifying at a few degrees below 0°. Lighter than water. Smells stronger than the acid. — Turns brown when strongly *heated.* Decomposed by *alcoholic potash.* Soluble in *alcohol.*

				Carius.
34 C	204	76·12	75 91
32 H	32	11 94	11·98
4 O	32	11·94	12·11
C⁴H⁵O,C³⁰H²⁷O³	268	100·00	100·00

Chlorine-nucleus C³⁰ClH²⁷.

Chloride of Cimicyl.

$$C^{30}ClH^{27}O^2 = C^{30}ClH^{27},O^2.$$
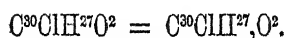
Carius. *Ann. Pharm.* 114, 154.

Cimicic acid in contact with pentachloride of phosphorus, gives off hydrochloric acid gas, becomes warm, and is converted into a colourless liquid. This, when treated with water, gives up chlorophosphoric acid, while chloride of cimicyl remains undissolved.

Colourless oil, solidifying to a non-crystalline mass at about the same temperature as cimicic acid. — It is not perceptibly altered by water, but is decomposed by *potash-ley.* With *alcohol* it forms cimicic ether.

Soluble in *ether.*

COMPOUNDS CONTAINING 32 AT. CARBON.

Primary Nucleus $C^{32}H^{22}$; *Oxygen-nucleus* $C^{32}H^{12}O^{10}$.

Hæmatoxylin.

$$C^{32}H^{14}O^{12} = C^{32}H^{12}O^{10},H^2O^2.$$
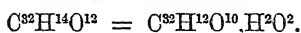
CHEVREUL. *Ann. Chim.* 82, 53, and 126; *Schw.* 8, 221 and 272.

O. L. ERDMANN. *J. pr. Chem.* 26, 193; *Ann. Pharm.* 44, 294; *Berz. Jahresb.* 23, 479.

F. LEBLANC. *Dumas, Traité de Chimie appliquée aux arts.* 8, 107.

O. HESSE. *J. pr. Chem.* 75, 218; abstr. *Chem. Centr.* 1859, 278; *Rép. Chim. pure*, 1, 191.—In detail and with additions, *Ann. Pharm.* 109, 332.

Hæmatin (Chevreul). *Chryshématine* (Leblanc). — Discovered by Chevreul; obtained pure by Erdmann. — Preisser's statements respecting it (*Rev. scient.* 18, 43; abstr. *J. pr. Chem.* 32, 135) were not confirmed by Bolley (*Ann. Pharm.* 62, 129).

Occurrence. In logwood, *Hæmatoxylon campechianum*, (*Handbuch*, viii., *Phytochem.* 8) (Chevreul). Teschemacher found in logwood a crystalline mass; Schutzenberger & Paraf found in the vats in which the extract was kept, long needles of hæmatoxylin. — *Braziln* obtained by Chevreul (*Ann. Chim.* 66, 226) from Pernambuco wood (from *Cæsalpinea echinata*), and Brazil-wood (from *Cæs. vesicaria, C. Sapun* and *C. crista*) (*Handbuch, loc. cit.* 8) appears to be impure hæmatoxylin, and, according to Schutzenberger & Paraf, behaves like hæmatoxylin when heated with ammonia. On the reactions of the decoction of Pernambuco wood, see Bonsdorff (*Ann. Chim. Phys.* 19, 283; *Schw.* 35, 329) and Pleisch (*Zeitschr. Phys. Math.* 10, 388).

Preparation. From the dry commercial extract of logwood. The pulverised extract is mixed with a large quantity of sand, drenched with 5 or 6 vols. of ether (containing water: *Hesse*), left to stand for several days, and frequently agitated, the solution then decanted, and the residue several times subjected to the same treatment. The brownish yellow solutions are distilled (to recover the ether) till the residue has become syrupy, whereupon it is mixed with water, and left to crystallise in a loosely covered vessel. The crystals, of which the mother-liquor yields an additional quantity, are washed with cold water and pressed (Erdmann); they may be obtained colourless by recrystallisation from water containing a small quantity of sulphurous acid (Leblanc), bisulphite of ammonia, or bisulphite of soda (Hesse).

Respecting the formation of crystals, see also the behaviour of hæmatoxylin to water. — 1 lb. extract of logwood yields from 1½ to 2 oz. of crystals of hæmatoxylin (Erdmann).

Properties. The hydrated crystals become anhydrous when heated to 100°—120°, but do not melt at that temperature, provided the water be driven off slowly (Erdmann, Leblanc). — Taste, very much like that of liquorice; very persistent; not at all bitter or astringent (Erdmann). Rotatory power of the aqueous solution, to the right; $[\alpha]j$ about $=$ 92° (Hesse).

			Erdmann. *mean.*		Hesse.
32 C	192	....	63·57	.... 63·47	.... 63·21
14 H	14	....	4·64	.... 4·68	.... 4·68
12 O	96	....	31·79	.... 31·85	.... 32·11
$C^{32}H^{14}O^{12}$	302	....	100·00	.... 100·00	.... 100·00

Erdmann at first gave the formula $C^{40}H^{17}O^{15}$, but was afterwards convinced of the correctness of the above, which was proposed by Gerhardt. Hæmatoxylin appears to be related to hæmatein in the same manner as mannite to lævoglucose, or as alcohol to aldehyde (Kr.).

Amorphous Hæmatoxylin. — A solution of crystallised hæmatoxylin in aqueous hyposulphite of soda deposits amorphous hæmatoxylin on cooling. — On dropping into a solution of hæmatoxylin in aqueous borax [(see below), or in aqueous bisodic phosphate], a concentrated aqueous solution of chloride of sodium, (or of chloride of potassium, chloride of ammonium, or ferrocyanide of potassium, but not of carbonate of soda, sulphate of soda, or oxalate of potash), amorphous, spherical masses are separated, which, on stirring the liquid, unite into a ropy mass having a silky lustre. This amorphous hæmatoxylin dissolves readily in boiling water or alcohol, and separates from these solutions on cooling; still in the amorphous state; but on addition of a drop of hydrochloric acid, it is deposited in mostly bihydrated crystals. The amorphous hæmatoxylin precipitated by bisulphite of ammonia from a solution of borax-hæmatoxylin likewise dissolves on boiling, and separates on cooling, still in the amorphous state; but if it be dissolved by continually dropping bisulphite of ammonia into the liquid, crystals soon separate out. Hence it appears that hæmatoxylin dissolves in the above alkaline liquids in the amorphous state, but is reconverted into crystalline hæmatoxylin by free acids (Hesse).

Decompositions. 1. Hæmatoxylin exposed to sunshine in a closed glass vessel, acquires a reddish colour without perceptible change of composition. This coloration likewise take place in a vacuum (Erdmann). — 2. When *heated*, it decomposes, without any trace of sublimation, and leaves a large quantity of charcoal (Erdmann). — 3. In dry *oxygen-gas*, it remains unaltered, provided the gas is free from ammonia (Erdmann) and from ozone (Schönbein). An aqueous solution of hæmatoxylin does not become coloured in oxygen gas free from ammonia (Erdmann).

4. In contact with moist, strongly *ozonised air*, it soon acquires a rusty brown colour, becomes moist, and deliquesces to a brown tenacious mass, which then becomes more mobile, lighter, and finally colourless, and contains free oxalic acid. — Aqueous hæmatoxylin is decomposed in like manner when ozonised air is passed through it. Filtering paper soaked in an ethereal solution of hæmatoxylin, and exposed to ozonised air, quickly assumes a reddish yellow colour, changing to brown-red, but ultimately becomes colourless, and acquires an acid taste (Schönbein).

The tints which moist, or aqueous hæmatoxylin, acquires in contact with the peroxides of manganese (violet), nickel (violet), lead (yellow-brown), and with ferric salts (dark violet), — also the red colouring imparted to it by chromic acid, hypochlorites and permanganate of potash, are attributed by Schönbein to negatively

active ozonised oxygen existing in these compounds.— On the other hand, peroxide of hydrogen or ozonised oil of turpentine (xiv, 257), in the entire absence of alkalis, does not colour aqueous hæmatoxylin immediately, and but feebly on standing ; moreover, the presence of peroxide of hydrogen is recognisable in the liquid, together with unaltered hæmatoxylin, even after several days, because, according to Schonbein, the oxygen, which is here positively active, is not able to oxidise the hæmatoxylin. — The brown-red coloration which moist or aqueous hæmatoxylin acquires in oxygen free from ozone (but containing ammonia ? Kr.), in the dark, or much more quickly when exposed to light, is supposed to arise from oxidation accompanied by the formation of peroxide of hydrogen, although the peroxide of hydrogen cannot be recognised unless alkalis are likewise present.   In this oxidation, as in many allied phenomenæ, ordinary oxygen is resolved into positively and negatively active oxygen, the former of which determines the formation of peroxide of hydrogen, while the latter determines the oxidation of the hæmatoxylin (Schonbein, *J. pr. Chem.* 81, 257).

5. Hæmatoxylin dissolves in aqueous *ammonia*, first with rose-red, then with fine purple-red colour ; and if its solution is evaporated with as little contact of air as possible, it crystallises, for the most part unaltered, leaving a dark red mother-liquor.   When exposed to the air, the ammoniacal solution quickly absorbs oxygen, becomes darker in colour, finally black-red, and then contains hæmateïn, which may either be precipitated from the solution by acids, or crystallised as an ammonia-compound by evaporation (Erdmann). — Formation of hæmatein :

$$C^{32}H^{11}O^{12} + 2O = C^{32}H^{12}O^{12} + 2HO.$$
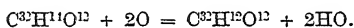
When hæmatoxylin is heated to 100° for 48 hours with strong aqueous ammonia, in a vessel which prevents the air from having access to it, the solution, which is violet at first, gradually becomes whitish yellow, but quickly recovers its violet colour when the tube is opened, so that the white product cannot be obtained unchanged, for analysis.   It contains nitrogen, but not in the form of ammonia ; it is colourless, very slightly soluble in water, soluble in hydrochloric acid, precipitable in white flocks by ammonia, soluble in alcohol and ether. This body is probably *hæmatinamide* = $C^{32}H^{14}O^{12},2NH^3$ (Schützenberger & Parafin, *Mulh. Soc. Bull.* 1861, 511).

6. Hæmatoxylin is but slightly coloured by boiling with *potash-ley* which has been de-aërated by boiling, or with aqueous *carbonate of soda*, in a space filled with hydrogen, and may be almost wholly recovered from the red liquid thus produced, by neutralising with hydrochloric acid (Hesse). — Aqueous hæmatoxylin in contact with potashley in a vessel which excludes it from the air, acquires a light violetblue colour, which on admission of oxygen, or on leaving the solution in contact with the air, becomes darker, then purple-red, brown-yellow, and finally dirty-brown.   The last-formed product is not precipitable by acids, but, after acidulation with acetic acid, it may be precipitated by acetate of copper.   When an alcoholic solution of hæmatoxylin is exposed to the air in contact with alcoholic potash, black-blue flakes are deposited, free from carbonate of potash (Erdmann). — A solution of hæmatoxylin in contact with the air is coloured by carbonate of potash, baryta-water, or carbonate of lime, in the same manner as by caustic potash (Erdmann), also by bicarbonate of lime ; consequently the alcoholic tincture of freshly hewn logwood will indicate the presence of the smallest quantity of bicarbonate of lime in water (Dupasquier, *J. Chim. méd.* 22, 542).

7. When *chlorine* is passed into aqueous hæmatoxylin, a yellow-brown liquid is formed, which becomes darker on evaporation, and deposits black amorphous films, not precipitable from the alkaline solution by acids (Erdmanns). — 8. Aqueous hæmatoxylin is reddened by very dilute *nitric acid* and decomposed by the concentrated acid, even in the cold, with violent effervescence and formation of oxalic acid (Erdmann). — 9. It dissolves in cold *oil of vitriol*, with brown-yellow colour, and apparently unaltered; but the solution, when left to itself or heated, deposits brown or black substances (Erdmann). — A mixture of common and Nordhausen sulphuric acid does not form a conjugated acid with hæmatoxylin.

10. Aqueous hæmatoxylin reduces *oxide of lead* to the metallic state on standing; *nitrate of silver* at ordinary temperatures; and *terchloride of gold* when heated. It blackens *mercuric oxide* when heated with it; reduces *mercurous nitrate* imperfectly; does not reduce mercuric chloride or *bichloride of platinum* (Erdmann). It does not reduce *potassio-cupric tartrate.* — 11. A small quantity of *potash-iron-alum* (v. 279) separates from aqueous hæmatoxylin, on warming or standing, a black-violet precipitate, which contains hæmateïn and ferrous or ferroso-ferric oxide, and forms, with excess of the iron-alum, a deep violet solution, which becomes greenish on exposure to the air (Erdmann, *J. pr. Chem.* 76, 393).

12. Aqueous *chromic acid* dissolves hæmatoxylin, with violent effervescence, forming a brown solution.

By boiling for a day with *hydrochloric acid*, by prolonged contact with yeast at 30°, or with *emulsin* at 45°, it is coloured, but remains for the most part unaltered (Hesse).

Combinations. With Water. Hæmatoxylin is obtained from its solutions as (amorphous or as) bi- or sex-hydrated hæmatoxylin.

A. *With 2 at. Water.* An aqueous solution of hæmatoxylin saturated at the boiling heat, and left to cool in a closed vessel, deposits this hydrate long before complete cooling, in light yellow, hard, granular crusts, which assume a flesh-red colour, more quickly than the sexhydrated crystals, in diffused daylight, and immediately in sunshine (Erdmann). The sex-hydrated crystals which separate from solutions of hæmatoxylin containing salts, sometimes change into the bi-hydrated crystals while still immersed in the liquid (Hesse). The bi-hydrated crystals belong to the right prismatic system, exhibiting a tetrahedron *a* (fig. 72), having its horizontal edges replaced by *p* (*Fig.* 63), also a horizontal prism *y*. All the faces, except *p*, are much curved (Naumann, *J. pr. Chem.* 75, 228.)

			Erdmann. mean.	Leblanc.
Dried in the air, or over oil of vitriol.				
32 C	192	60	59·71	60·0
16 H	16	5	5·02	4·9
14 O	112	35	35·27	35·1
$C^{32}H^{14}O^{12}$,2Aq.	320	100	100·00	100·0

			Erdmann.	Leblanc.	Hesse.
$C^{32}H^{14}O^{12}$	302	94·38			
2HO	18	5·62	6·25	5·6	5·61
$C^{32}H^{14}O^{12}$,2HO	320	100·00			

B. *With 6 at. Water.* — Colourless or dazzling white crystals
(Hesse). Transparent prisms, having a strong lustre and pale straw-
yellow to honey-yellow colour (Erdmann); they belong to the square
prismatic system. *Fig.* 29, with α from *Fig.* 27; e : e = 124° (Kopp).
Rammelsberg observed the same crystals without α, but with p
(*Fig.* 30). A face of e is in general very predominant. e : e = 123° 25'
(nearly); e : q = 118° 6'; e : p = 131° 30' (Rammelsberg). See also
Teschemacher and C. Wolff (*J. pr. Chem.*, 26, 195). — May be rubbed to a
white or pale-yellow powder. The crystals, if kept in badly-closed
vessels, effloresce in dry air or in a vacuum (perhaps from conversion
into bi-hydrated hæmatoxylin); when quickly heated to 100°, they
melt in their water of crystallisation to a reddish mass, and give off
all their water (the last portions slowly) between 100° and 120°
(Erdmann).

		Crystals.			Erdmann.
32 C	....	192	....	53·93	.... 53·78
20 H	....	20	....	5 62	.... 5·78
18 O	... .	144	....	40·45	.... 40·44

$C^{32}H^{14}O^{12}$,6Aq.	356	....	100·00	.. ... 100 00

			Erdmann.	Leblanc.	Hesse.
$C^{32}H^{14}O^{12}$	302	. ...	84·83	....		
6HO	54	.	15·17	16·32	. .. 15 00	.... 15·30

$C^{32}H^{14}O^{12}$,6Aq	356	.... .	100 00	....

C. *Aqueous Solution.* — Hæmatoxylin dissolves slowly and sparingly
in cold water, very abundantly in boiling water (Erdmann).

Borax and Hematoxylin. — Hæmatoxylin dissolves in a cold saturated
aqueous solution of borax more abundantly than in water; a warm
solution takes up so much that it becomes syrupy. No crystals are
obtained on evaporating the liquid. The borax-solution, by dissolving
the hæmatoxylin, loses its alkaline reaction, becomes bluish-fluorescent,
and is no longer precipitable by absolute alcohol or ether-alcohol;
it rotates a polarised ray, sometimes strongly to the right, sometimes
not at all, or very slightly to the left. On dropping an acid into the
solution of borax-hæmatoxylin, it becomes violently agitated, and
solidifies in from 10 to 20 seconds to a thick crystalline pulp; certain
saline solutions dropped into it precipitate amorphous hæmatoxylin
(Hesse, p. 288).

An aqueous solution of *bisodic phosphate* dissolves a large quantity
of hæmatoxylin without losing its alkaline reaction (Hesse). — Hæma-
toxylin dissolves sparingly in solution of *chloride of sodium*, more easily
in aqueous *chloride of barium*, without forming a precipitate (Hesse).
According to Erdmann, it colours chloride of barium red, and forms after a while a
red precipitate.

Baryta-water added to aqueous hæmatoxylin, free from air, throws
down a white or pale-blue precipitate, which, on exposure to the air,
becomes dark-blue and subsequently brown-red (Erdmann). — Solution
of *alum* forms no precipitate, even when added only in small quantity,
but colours the solution light-red (Erdmann). From an aqueous solu-
tion of hæmatoxylin mixed with excess of soda-ley, aluminate of soda
throws down a copious precipitate insoluble in soda-ley (Plessy, *Dingl.*
143, 158).

Aqueous hæmatoxylin forms with *neutral* or *basic acetate of lead*, a pure white precipitate, which quickly turns blue when exposed to the air (Erdmann).—It forms a rose-coloured precipitate with *proto-chloride of tin.* — With *sulphate* and *acetate of copper*, it forms dirty greenish-grey precipitates, which quickly change to dark-blue, and when dried exhibit a bronze colour and metallic lustre (Erdmann).

Hæmatoxylin dissolves in *alcohol* more readily than in *ether*. From the ethereal solution it does not crystallise by evaporation, except in presence of water. — With solution of *isinglass*, it forms a slight white precipitate, which disappears when the liquid is heated, and reappears on cooling (Erdmann).

Hæmateïn.

$$C^{32}H^{12}O^{12} = C^{32}H^{12}O^{10},O^2.$$
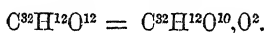
O. L. ERDMANN.   *J. pr. Chem.* 26, 205 ; 76, 394.
O. HESSE.   *Ann. Pharm.* 100, 337.

(Formation, p. 289.)

Preparation.   20 gr. hæmatoxylin is drenched in a porcelain basin with a quantity of ammonia sufficient to dissolve it, the liquid being stirred, and the solution assisted, if necessary, by warming, as long as any hæmatoxylin remains in excess.   The solution is left exposed to the air for some days, with frequent stirring and occasional addition of ammonia, in sufficient quantity to make it always smell of that alkali, till it has acquired a dark cherry-red colour, and when mixed with acetic acid, deposits hæmateïn in the form of a rust-brown precipitate. If left to itself, it soon deposits granular crystals of hæmateïn-ammonia, which may be separated from the mother-liquor by rapid filtration, washing with a small quantity of cold water, and pressing between bibulous paper, and then dried by exposure to the air.   A further quantity of hæmateïn-ammonia may be obtained from the mother-liquors by spontaneous evaporation, with addition of ammonia; but the liquid, if left to evaporate by itself, dries up to a blackish-green mass containing hæmateïn with only a small quantity of ammonia (Erdmann).   Hesse dissolves 10 gr. hæmatoxylin in a quantity of warm aqueous ammonia less than that which is required for the production of hæmateïn-ammonia; filters the solution into a flat dish ; and leaves it for two or three days, frequently adding small quantities of ammonia. After a considerable time, amorphous substances are deposited on the crystals which first separate.

From hæmateïn-ammonia, hæmateïn is obtained, either by decomposing the compound with acetic acid, dissolving the precipitate in boiling water, and concentrating the solution, whereupon it separates in laminæ,—or by heating to 120° (Erdmann).   To obtain a residue of constant weight and free from ammonia, the heat must be raised to 130° (Hesse).

Properties.   Hesse's hæmateïn forms a black-violet powder with greenish iridescence, and very hygroscopic. — Erdmann's hæmateïn, which may be regarded as a hydrate compared with that of Hesse, exhibits, when precipitated from the ammoniacal solution by acetic acid, and dried, a dark-green colour and metallic lustre, and yields by tritu-

ration, a powder of a pure light-red colour. From the aqueous solution it separates by evaporation, in dirty-green, metallically-lustrous laminæ, but from a solution highly concentrated and then cooled, it is deposited in crystalline grains, or as a red-brown jelly, in which reddish scales may be distinguished by the microscope.

		at 130°.				Hesse.
32 C	. ...	192	....	68·08	. . . .	67·66
10 H	....	10	....	3 54	....	3 50
10 O	.. ..	80	.. ..	28 38	. .	28·84

$C^{32}H^{10}O^{10}$	....	282	....	100·00	....	100 00

						Erdmann.
		at 100—120°.				*mean.*
32 C	....	192	....	64	....	62·65
12 H	....	42	....	4	....	4·16
12 O	....	96	....	32	. ...	33·19

$C^{32}H^{12}O^{12}$	....	230	....	100	....	100 00

Erdmann analysed, with nearly equal results, hæmateïn crystallised from water, precipitated by acetic acid, and obtained by heating hæmateïn-ammonia. Hesse's formula is based upon the loss of weight which hæmateïn-ammonia suffers when heated.

Decomposition. Hæmateïn leaves a bulky cinder when *ignited.* — It dissolves in *nitric acid* with purple-red colour, which soon passes into yellow. — The solutions in aqueous *ammonia* and *potash* turn brown when exposed to the air. — Hæmateïn-ammonia immediately reduces the metal from *nitrate of silver,* more slowly from *mercurous nitrate.* — Hæmateïn placed in contact with *zinc* and aqueous *hydrochloric acid,* dissolves, with light yellow-brown colour, and the filtered solution deposits a small quantity of a violet precipitate containing zinc; the same solution yields with alkalis a copious white or pale violet precipitate, no longer the brown-violet precipitate of hæmateïn-solutions, so that it appears to contain, no longer hæmateïn, but probably hæmatoxylin. — Hæmateïn is not reduced to hæmatoxylin by *hydrosulphuric acid* or *hydrosulphate of ammonia* (Erdmann).

Combinations. Hæmateïn dissolves slowly in cold *water,* more easily in boiling water, forming a yellow-brown solution. It dissolves in dilute *hydrochloric* and *sulphuric acids,* with red colour, changing to yellow on dilution with water; with *oil of vitriol* it forms a brown solution, from which it is precipitated by water; in *acetic acid* it dissolves less freely than in mineral acids. — Its aqueous solution becomes lighter in colour when *hydrosulphuric acid* gas is passed through it, but recovers its original colour when the hydrosulphuric acid is evaporated, and on drying up leaves the hæmateïn in its original state (Erdmann).

Hæmateïn-ammonia.—Hæmateïn dissolves in ammonia with splendid purple-red colour. For the mode of preparation, see page 292. The compound is a violet-black, granular powder, consisting of microscopic, transparent, violet-coloured, four-sided prisms. In the dry state, it remains unaltered over oil of vitriol or in a vacuum, but if moist, it readily gives off ammonia, which is also completely expelled by heat. It dissolves in water with dark purple colour, in alcohol with brown-red colour, changing to purple-red on addition of water.—The solutions give off ammonia when evaporated (Erdmann).

a. The compound examined by Erdmann appears to contain 1 at. hæmateïn to 2 at. ammonia (Hesse).

				Erdmann.
				mean.
32 C	192	57·49	56·26
2 N	28	8·38	6·82
18 H	18	5·39	5·17
12 O	96	28·74	31·75

$$C^{32}H^{12}O^{12},2NH^3 \dots \dots \dots 334 \dots \dots 100·00 \dots \dots 100·00$$

b. The crystals retain different quantities of water, according as they have been dried for one or more hours over oil of vitriol, or merely pressed between paper. After drying for an hour between paper over oil of vitriol, they exhibited the composition $C^{32}H^9(NH^4)O^{10},8HO$, and gave off, at 130°, 19·78 p. c. water, after deducting the ammonia which escaped at the same time (calc. 19·11 p. c. HO). The crystals prepared by different methods exhibit the same composition, excepting in so far as they may contain a larger or smaller quantity of water (Hesse).

				Hesse.
32 C	192	51·75	51·68
N	14	3·77	3·76
21 H	21	5·66	5·89
18 O	144	38·82	38·67

$$C^{32}H^9(NH^4)O^{10},8HO \dots 371 \dots \dots 100·00 \dots \dots 100·00$$

Hæmateïn-ammonia is precipitated from its aqueous solution in the amorphous state by chloride of sodium, ammonium, or potassium. With bisulphite of ammonia it forms a jelly, which dissolves on boiling, forming a clear yellow solution. It is not altered by hyposulphite of soda (Hesse).

Hæmateïn dissolves in *potash-ley* with blue colour, changing to red and brown in contact with the air (Erdmann).

Aqueous hæmateïn-ammonia throws down from *chloride of barium* a dark purple-red precipitate, the colour of which, changes to dirty brown in contact with the air. With excess of *alum-solution*, it forms a dark red-violet solution, without precipitation; but when mixed with a small quantity of alum, till it acquires a red colour and heated, it yields a deep violet-coloured precipitate (Erdmann).—With *nitrate of bismuth, sulphate of zinc,* and *protochloride of tin,* it forms violet precipitates (Erdmann).

Lead-compound of Hæmateïn.—Aqueous hæmateïn-ammonia forms with neutral acetate of lead, a dark blue precipitate, the liquid becoming acid in whatever manner the precipitation be performed. The precipitate is partially decomposed by washing, the wash-water becoming brown; after washing for a short time it contains (*a*) 50·78 p. c. lead-oxide; after longer washing, quantities varying from 43·6 to 51 p. c. (Erdmann).

						Erdmann.		
						a.	*b.*	*c.*
32 C	38·6	32 C	31·5	31·4	36·1	35·7
9 H	1·8	9 H	1·5	1·8	1·9	2·0
9 O	14·5	9 O	11·8	16·0	18·4	15·6
2 PbO	45·1	3 PbO	55·2	50·8	43·6	46·7

$C^{32}H^9PbO^{10},PbO$ 100·0 $C^{32}H^9PbO^{10},2PbO\dots$ 100·0 .... 100·0 .... 100·0 .... 100·0

Aqueous hæmateïn-ammonia forms with *ferrous chloride* a violet precipitate ; with *potash-iron-alum* a black precipitate (Erdmann).

Hæmateïn dissolves with red-brown colour in *alcohol*, sparingly and with amber-yellow colour in *ether* (Erdmann).

Primary Nucleus $C^{32}H^{24}$; *Oxygen-nucleus* $C^{32}H^{14}O^{10}$.

Beta-orsellic Acid.

$C^{32}H^{14}O^{14} = C^{32}H^{14}O^{10},O^{4}$; more correctly $C^{16}H^{7}O^{7},C^{16}H^{7}O^{7}$?

STENHOUSE. *Phil. Trans.* 1848, 69 ; *Ann. Pharm.* 68, 66.

Occurs in *Roccella tinctoria* from the Cape of Good Hope, and is extracted therefrom, but together with roccellinin, in the same manner as lecanoric acid from the *Roccella tinctoria* of South America (xii. 377. 3). The precipitate thrown down from the lime-extract by hydrocloric acid is a mixture of beta-orsellic acid and roccellinin ; on exhausting it repeatedly with water, the roccellinin remains undissolved, while the beta-orsellic acid crystallises from the filtrate.

The acid resembles lecanoric acid, and reacts like that acid with *chloride of lime*, and with *ammonia, baryta* and *lime.*—At 100° it contains, on the avarage, 60·14 p. c. C., 5·16 H., and 34·70 O, and has, therefore, in the free state, exactly the same composition as lecanoric acid (xii. 378) ; its baryta-salt has also the composition of lecanorate of baryta (49·46 p. c. C., 4·12 H., 18·52 BaO). The acid further resembles lecanoric acid in yielding orsellate of ethyl (xii. 373) when boiled with alcohol ; but it forms a black precipitate with neutral acetate of lead, whereas lecanoric acid is not precipitated by that salt. — Stenhouse assigns to beta-orsellic acid the formula $C^{34}H^{17}O^{15}$ Strecker's formula $C^{34}H^{16}O^{15}$ (*Ann. Pharm.* 68, 110\ contains 1 at. hydrogen less; he regards roccellinin as a product of the decomposition of beta-orsellic acid, formed, simultaneously with orsellic acid, according to the equation, $C^{34}H^{16}O^{15} = C^{16}H^{8}O^{8} + C^{18}H^{8}O^{7}$. On the other hand, Schunck (*Phil. Mag. J.* 33, 256) and Gerhardt (*Compt. chim.* 1149, 127 ; *Traité* 3, 797) regard beta-orsellic acid as identical with lecanoric acid, which view may, till further investigation, be regarded as the most probable (Kr.).

Gyrophoric Acid.

? $C^{32}H^{14}O^{14} = C^{16}H^{7}O^{7},C^{16}H^{7}O^{7}$.

STENHOUSE. *Phil. Trans.* 1849, 393 ; *Ann. Pharm.* 70, 218.

Obtained from the *Gyrophora pustulata* and *Lecanora tartarea* of Norway, in the same manner as lecanoric acid from *Roccella tinctoria* (xii, 377, 3).

Small, soft, colourless crystals, destitute of taste and smell. Does not redden litmus ; the solutions acquire an alkaline reaction on addition of mere traces of potash or ammonia.

Stenhouse.

a.		b.				
32 C	60·37	34 C	61·14 ...	60·81 ..	61·16	61·12
14 H	4·40	16 H	4·82 ...	4·90	5 20 ...	5·00
14 O	35·23	14 O	33·74 .	34·29	33 64	33 88
C³²H¹⁴O¹⁴	100·00	C³⁴H¹⁶O¹⁴	100·00 ..	100·00	100·00	100·00

a is the formula of lecanoric acid; b, that of evernic acid. Gerhardt (*Traité*, 3, 808) regarded gyrophoric as identical with one or the other of these acids. Stenhouse regards it as a peculiar acid, and assigns to it the formula C³⁶H¹⁸O¹⁵.

By boiling with *potash* or *baryta-water*, it is converted into a carbonate and orcin; but when boiled with a very small quantity of potashley, it yields an intermediate acid, which is distinctly sour, soluble in water, and crystallises differently from gyrophoric acid.

Gyrophoric acid is reddened by *chloride of lime*, the red colour not disappearing so quickly as in the case of lecanoric acid. — When exposed to the air, in contact with excess of *ammonia*, it is slowly converted into a purple colouring matter. — Gyrophoric acid boiled for several hours with strong *alcohol*, yields, together with small quantities of orcin and resin, an ethylic ether resembling orsellate of ethyl (xii. 373) in properties and composition (mean. 61·32 p. c. C., 6·25 H., and 32·43 O). With *wood-spirit*, the corresponding methylic ether is obtained.

Gyrophoric acid is nearly insoluble in *water*, even at the boiling heat. — It is also nearly insoluble in excess of cold aqueous *ammonia;* from the alcoholic solution it is precipitated by ammonia, without taking up any portion of that alkali. — It dissolves readily in excess of *baryta-water*, and is precipitated by acids without alteration. By passing carbonic acid into the solution, and boiling the precipitate with alcohol (as in the case of lecanorate of baryta, xii 379), a baryta-salt is obtained in small crystals, insoluble in cold alcohol; but the acid separated therefrom is different from gyrophoric acid in composition and in solubility.

Alcoholic gyrophoric acid does not precipitate an alcoholic solution of *neutral acetate of lead;* with the *basic acetate* it forms a precipitate of variable composition.

The acid dissolves with difficulty in *ether;* in boiling *alcohol* also it is much less soluble than lecanoric acid.

Appendix to Beta-orsellic and Gyrophoric Acids.

1. Roccellinin.

? C³⁶H¹⁶O¹⁴.
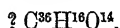
Stenhouse.   *Phil. Trans.* 1848, 71; *Ann. Pharm.* 68, 69.

Occurs, together with beta-orsellic acid, in *Roccella tinctoria* from, the Cape.

The extract of the lichen prepared with lime-water, deposits, on addition of hydrochloric acid, a mixture of beta-orsellic acid and roccellinin, which, after washing and drying, is continuously boiled with

alcohol, whereby the beta-orsellic acid is converted into orsellate of ethyl. The solution is evaporated to dryness; the orsellic ether is extracted from the residue by boiling water; and the roccellinin which remains is purified by recrystallisation from a large quantity of strong alcohol.

Fine capillary crystals, having a silky lustre.

							Stenhouse.
							mean.
36 C	....	216	....	62·79	....	62·58
16 H	....	16	.. ..	4·65	....	4·82
14 O	....	112	... .	32 56	.. ..	32·60
$C^{36}H^{16}O^{14}$	....	344	....	100·00	....	100·00

So according to Strecker (*Ann. Pharm.* 68, 110) who regards roccellinin as a product of the decomposition of beta-orsellic acid. Stenhouse gives the formula $C^{38}H^{17}O^{15}$ (see page 295).

Roccellinin treated with *solution of chloride of lime* acquires a permanent greenish yellow colour. — When suspended in water through which *chlorine gas* is passed, it becomes yellowish without taking up chlorine or undergoing any further alteration. — When boiled with *potash* or *baryta-water*, it does not suffer decomposition, or yield carbonate of baryta. — Hot *nitric acid* decomposes it, with formation of oxalic acid.

Roccellinin does not dissolve in *water*, either cold or hot. — It dissolves easily in aqueous *ammonia*, and remains free from ammonia when the solution is evaporated. It dissolves in *potash* and *soda-ley*. When boiled with *carbonate of baryta*, it forms a crystallisable salt, differing in composition according to the concentration of the solution. It does not precipitate *neutral* or *basic acetate* of lead, or *ammoniacal nitrate of silver*.

It dissolves very sparingly in cold *alcohol* and *ether*, requiring also a large quantity of boiling alcohol to dissolve it. It does not form an ether when boiled with alcohol saturated with hydrochloric acid gas.

2. Ceratophyllin.

O. HESSE. *Ann. Pharm.* 119, 365.

Occurs, together with physodin (xv, 57) in *Parmelia physodes*. Already described in the Addenda to vol. xv (p. 534).

3. Variolarin.

ROBIQUET. *Ann. Chim. Phys.* 42, 236.

Occurrence. In *Variolaria dealbata.*

When the lichen is exhausted with boiling alcohol, as described under *orcin* (xii., 353, 1), the extract freed from orcin by water, and then treated with ether, and the ethereal solution evaporated, a crystalline residue is left, which may be freed from soft resin by cold alcohol, and dissolved in boiling alcohol. The alcoholic solution, as it cools,

deposits long needles of *variolarin.* —This substance melts at a moderate heat to a resin, which solidifies in a lamino-crystalline mass. When strongly *heated*, it boils and gives off a strong-smelling volatile oil, after which a portion sublimes in white needles.

Variolarin is not coloured either by *alkalis* or by *acids.* It dissolves readily in *alcohol* and in *ether.*

Appendix to vol. xiii. p. 325.

Parellic Acid.

$$C^{18}H^6O^8 \ = \ C^{18}H^6O^4,O^4.$$
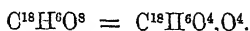
ED. SCHUNCK. *Ann. Pharm.* 54, 257, and 274.—Preliminary Notice, *Ann. Pharm.* 41, 161.

Parellin. Sometimes obtained in the preparation of lecanoric acid (xii., 377) from *Lecanora Parella.*

From the mixture of lecanoric and parellic acids obtained according to xii. 377, baryta-water precipitates insoluble parellate of baryta, from which the parellic acid may be separated by decomposition with hydrochloric acid. The acid is purified by washing with water and recrystallisation from alcohol. When the lichen is exhausted with boiling alcohol, the lecanoric acid taken up thereby may be converted by prolonged boiling of the solution into orsellic ether (xii, 373), and on evaporating to dryness and extracting the ether from the residue with boiling water, parellic acid remains undissolved.

Properties. The hydrated crystallised acid is rendered anhydrous by heating to 100°. — Tastes bitter when chewed, or in alcoholic solution. The alcoholic solution reddens litmus.

		Dried.			Schunck.		
18 C	108		60·67		59·85		61·00
6 H	6		3·37		3·37		3·42
8 O	64		35·96		36·78		35·58
C¹⁸H⁶O⁸	178		100·00		100·00		100·00

The above is Gerhardt's formula (*Traité,* 3, 804) ; Schunck's formula is C²¹H⁷O⁹. — According to Gerhardt, parellic acid is probably a decomposition-product of lecanoric acid, produced, together with orcin, according to the equation, C³²H¹⁴O¹⁴ = C¹⁸H⁶O⁸ + C¹⁴H⁶O⁴ + 2HO.

Decompositions. 1. When *heated* in a tube, it melts and yields an oily distillate, in which a formation of needles takes place; the distillate often forms a crystalline solid on cooling. — 2. Heated on platinum foil, it melts, swells up, becomes brown, and burns without leaving a residue. — 3. Slowly decomposed by boiling with *water*; the yellow solution leaves a yellow, amorphous, bitter substance when evaporated. — 4. When heated with *nitric acid*, it evolves red vapours, and is converted into oxalic acid. — 5. An ammoniacal solution of *parellic acid* is coloured yellow by boiling, becomes brown in the air, and leaves, on evaporation, a brown, acid varnish, from an aqueous

solution of which, a brown or grey precipitate is thrown down by neutral acetate of lead, sesquichloride of iron, and sulphuric acid. — 6. Decomposed by boiling with excess of *caustic potash*, and with *lime-* or *baryta-water*. When baryta-water is used, the baryta-salt thrown down at first is dissolved by boiling, without being again precipitated on cooling; acids do not then throw down parellic acid, or only traces of it, but separate, after some hours, small shining crystals, which melt in boiling water, afterwards dissolve, and do not again crystallise. These crystals are obtained again by evaporation of their easily formed solution in cold alcohol : their solution in baryta-water yields carbonate of baryta when boiled. — If the boiling be continued after the acid has been dissolved in baryta-water, the solution acquires a yellow colour, and throws down carbonate of baryta, whereupon, after separation of the baryta, no crystals are formed, but a brown bitter extract is obtained. — 7. *Terchloride of gold* is not altered by aqueous parellic acid, and on boiling with an alkaline solution of the acid, it is more slowly reduced than by lecanoric acid.

Combinations. — *With Water.* — A. *Needles. Schunck's Mono-hydrated Parellic acid.* A boiling saturated alcoholic solution of parellic acid deposits on cooling, or on quick evaporation, long needles which lose 1 at. water at 100° (according to Schunck's formula $C^{31}H^7O^9$.)

	Needles.			Schunck. mean.
18 C	108	57·75		57·74
7 H	7	3·74		3·80
9 O	72	38·51		38·46
$C^{18}H^7O^9$	187	100·00		100·00

B. *Heavy Crystals.*—Schunk's bi-hydrated parellic acid. More dilute alcoholic solutions of the acids throw down, on cooling or slow evaporation, small, short, regular crystals, highly lustrous and having a high specific gravity. They lose 6·51 p. c. water at 100° (? 2 at. HO = 9·18 p. c.) and become opaque.

	Air-dried.			Schunck. mean.
18 C	108	55·10		55·94
8 H	8	4·08		3·99
10 O	80	40·82		40·07
$C^{18}H^6O^8$ + 2aq	196	100·00		100·00

C. *Aqueous solution.*—The acid dissolves with difficulty in hot water, and separates therefrom almost entirely on cooling, in light flakes.

Parellic acid expels carbonic acid from the carbonates of the alkalis.—It dissolves less easily in aqueous *ammonia* than in potash, and is left free from ammonia on evaporation.

In solution of *caustic potash* it swells up to a white jelly which gradually dissolves. It is precipitated from the solution (not previously boiled; see above) by acids, in the form of a thick jelly. Forms with *baryta-water* a white, insoluble salt. The same salt is precipitated in small cystalline needles on mixing an ammoniacal solution of the acid with chloride of barium.

Lead-salt. Alcoholic neutral acetate of lead throws down, from an

alcoholic solution of the acid, white flakes which contain 37·34 p. c. C., 2·73 H., 25·76 O., and 34·17 PbO.

The alcoholic acid does not precipitate *nitrate of silver;* the yellow precipitate appearing on addition of ammonia, is reduced by boiling.

Parellic acid dissolves in boiling *acetic acid* more freely than in water. It dissolves in *alcohol,* and is precipitated from the solution by water as a jelly. Soluble also in *ether.*

Primary Nucleus C^{32}H^{26}; *Oxyazo-nucleus* C^{32}NH^{17}O^8.

Cocaïne.

$$C^{32}NH^{19}O^8 = C^{32}NH^{17}O^8,H^2.$$
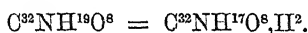
Alb. Niemann. *Inaugural-Dissertation über eine neue Base in den Cocablättern.* Göttingen 1860; *Pharm. Viertelj.* 9, 489; *N. Br. Arch.* 103, 129 and 291; abstr. *Chem. Centr.* 1860, 855; Preliminary Notice: *Ann. Pharm.* 114, 213; *J. pr. Chem.* 81, 129; *N. Ann. Chim. Phys.* 59, 479; *Rép. Chim. pure* 2, 373.

Wöhler & Lossen. *Ann. Pharm.* 121, 372; abstr. *Rép Chim. pure* 4, 367.

W. Lossen. *Inaugural-Dissertation über das Cocaïn.* Göttingen, 1862.

Discovered by Niemann in the leaves of *Erythroxylon Coca* (*Handbuch,* viii. *Phytochem.* 26) after Wackenroder (*N. Br. Arch.* 75, 23), Johnston (*Chem. Gaz.* 1853, 438), Gaedcke (*N. Br. Arch.* 82, 141) and Maclagan (*N. J. Pharm.* 29, 102) had unsuccessfully endeavoured to isolate the active principle of the leaves. Gaedcke designated the crystals obtained by dry distillation of the extract of coca-leaves, as *erythroxyline,* and found that they resembled caffeine in their behaviour towards nitric acid and ammonia.

Preparation. Coca-leaves are exhausted with rain-water at the temperature of 60° to 80°; the united extracts are precipitated with neutral acetate of lead and filtered; the filtrate is precipitated with a saturated aqueous solution of sulphate of soda, again filtered and concentrated; and the concentrated liquid, after being rendered slightly alkaline with carbonate of soda, is shaken 4 or 6 times with fresh portions of ether. The greater part of the ether is distilled off; the residue allowed to evaporate spontaneously; and the impure cocaïne remaining behind is freed from a part of the colouring matter by trituration with cold water,—after which a solution in hydrochloric acid is placed, in a thin layer, in a Graham's dialyser of parchment-paper, when, on thrice renewing the water in the outer vessel, most of the cocaïne diffuses in three days, while a large quantity of colouring matter is left in the inner vessel. The cocaïne is again separated from the solution, dissolved in alcohol, acidified with acetic acid, and left to evaporate, either spontaneously or over oil of vitrol. Cocaïne free from acetic acid remains behind, and is extracted from the residue by ether, whilst foreign substances in combination with acetic acid are left undissolved in the form of greasy drops (Lossen).

2. Chopped coca-leaves are digested for 4 days at a temperature of 40° in alcohol of 85 p. c. with which $\frac{1}{25}$th of oil of vitrol is mixed. The leaves are pressed, and the press-cake is moistened with alcohol and again pressed. The filtered extracts are shaken with excess of thin milk of lime, and after 24 hours, filtered and neutralised with dilute sulphuric acid. After distilling off most of the alcohol. the residue is evaporated to a syrup, or until the alcohol is all driven off, and poured into 20 times its bulk of water. The black-green resin hereby thrown down is removed by pouring off and filtering the liquid, which is then rendered alkaline with carbonate of soda, and shaken with ether so long as anything is taken up. By distillation and spontaneous evaporation of the ether, impure cocaïne is left behind, and is then dissolved in ether and shaken with water containing sulphuric acid. The ether, holding the greater part of the colouring matter in solution is removed, and the subjacent solution of sulphate of cocaine is precipitated with carbonate of soda. The precipitate is collected and purified by triturating it with a little strong alcohol, which first dissolves the colouring matter; it is then washed and recrystallised from alcohol (Niemann). The yield of impure cocaine amounts to $\frac{1}{4}$ p. c. of the leaves.

Properties. Cocaïne is obtained from an alcoholic solution to which water has been added (when pure also from ether-alcohol : *Lossen*), in large, colourless, transparent prisms belonging to the oblique prismatic system, and hemimorphous. Dominant form a horizontal prism formed of the faces *t, i, f.* (*Fig.* 97), terminated on the right by a hemidome *h* (to the front below and back above), on the left by a hemidome *α* (Fig 99) derived from another octahedron. $t : i = 106°$ 15'; $t : f$ (behind) $= 60° 1'$; $t : h = 114° 18'$; $t : α = 34° 30'$. Cleavable parallel to *h* (v. Fritzsch).

Cocaïne melts at 98°, and solidifies, on cooling, to a transparent, amorphous mass, which, after a while, becomes white and crystalline. When cautiously heated, a small portion appears to sublime. — Taste bitter and benumbing; afterwards cooling. Reaction alkaline (Niemann, Lossen).

			Crystals.					Niemann.
32	C	192	....	66·44	....	66·8	....	66·8
	N	14	....	4·84	....	5·4	....	
19	H	19	....	6·57	....	7·1	....	7·5
8	O	64	....	22·15	....	20·7		
	$C^{32}NH^{19}O^8$	289	....	100 00	....	100·0	....	

Niemann and Lossen give for cocaïne the formula $C^{32}NH^{20}O^8$; for ecgonine Lossen adopts the formula $C^{18}NH^{16}O^6$. Now since both formulæ contain an uneven number of nitrogen- + hydrogen-atoms, they either require to be doubled (as in the case of other alkaloïds), or the bases must be supposed to contain an atom more (so according to Limpricht, *Lehrbuch*, 1.195), or an atom less of hydrogen, a question on which the analyses are not sufficiently decisive. Preference is here given to the latter view (Kr.).

Decompositions. 1. Cocaïne *heated* above its melting point assumes a darker colour, creeps up the sides of the tube, evolves ammoniacal vapours, and carbonises (Niemann). — 2. When heated on platinum foil, it takes fire and *burns* with a luminous flame (Niemann). — 3. Dissolves in cold *oil of vitriol* without coloration, and carbonises when

heated (Niemann). — 4. Heated to 100° with concentrated *hydrochloric acid*, especially in a sealed tube, it splits up into benzoic acid, which separates in the form of an oil, and hydrochlorate of ecgonine (Wöhler & Lossen):

$$C^{32}NH^{19}O^3 + 2HO = C^{14}H^6O^4 + C^{18}NH^{15}O^6.$$
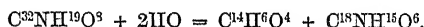
Very weak hydrochloric acid, boiled for several hours with cocaïne, emits an odour of benzoic acid, but leaves the greater part unchanged; stronger hydrochloric acid effects the decomposition over the water-bath (Lossen).

Combinations. Cocaïne dissolves in 704 parts of *water* at 12°, and rather more freely in hot water (Niemann).

It dissolves easily in dilute *acids*, forming crystallisable salts. Aqueous caustic ammonia and carbonate of ammonia throw down from an aqueous solution of hydrochlorate of cocaïne, white precipitates readily soluble in an excess of the precipitant. Caustic potash precipitates cocaïne, but a large excess redissolves it. The precipitate produced by carbonate of soda becomes crystalline on standing in the liquid, and does not dissolve in an excess of the precipitant. Carbonates and phosphates of the alkalis do not precipitate the solution. Iodine-water produces a scarlet-brown, biniodide of potassium a copious brown-red precipitate. The solution is not altered by tartar-emetic; it is rendered slightly turbid by sulphocyanide of potassium (Niemann).

Sulphate of Cocaïne. — The solution obtained by neutralising cocaïne with dilute sulphuric acid, dries up, over oil of vitriol, to a colourless varnish, in which colourless prisms, permanent in the air, are formed on standing (Niemann, Lossen).

Hydrochlorate of Cocaïne. — Cocaïne absorbs hydrochloric acid gas, with considerable development of heat, and melts; 100 parts of cocaïne take up in this way 13·57 parts of hydrochloric acid (calculation for C³²NH¹⁹O⁸ = 12·63 pts. HCl). The amorphous mass becomes white and crystalline on standing. It dissolves easily in water, with acid reaction. — From a solution of cocaïne in dilute hydrochloric acid, long delicate crystals are obtained, which are permanent in the air and very bitter (Niemann). An alcoholic solution yields, on evaporation over oil of vitriol, perfectly transparent, short prisms, with perpendicular end-faces; they scarcely diminish in weight at 120° (Lossen).

				Lossen.
C³²NH¹⁹O⁸	289·0	88·78		
HCl	36·5	11·22		10·75
C³²NH¹⁹O⁸,HCl	325·5	100·00		

Nitrate of Cocaïne. Amorphous mass, which becomes crystalline by standing over oil of vitriol, and deliquesces again in the air. Cocaine is not decomposed by fuming nitric acid (Niemann).

Protochloride of tin throws down, from hydrochlorate of cocaïne, a dense, white, curdy precipitate, soluble in a large quantity of nitric acid. *Chloride of mercury* and *iodide of mercury and potassium* precipitate a large quantity of flakes soluble in hydrochloric acid and in chloride of

ammonium; those produced by the former are easily soluble also in alcohol (Niemann).

Chloroplatinate of Cocaïne. — Bichloride of platinum produces, with hydrochlorate of cocaïne, a dirty grey-yellow (Niemann), white-yellow flocculent precipitate (Lossen), which soon becomes crystalline, and disappears on warming; it is slightly soluble in hydrochloric acid.

Chloro-aurate of Cocaïne. — Terchloride of gold also throws down from very dilute hydrochlorate of cocaïne, pale-yellow, amorphous flakes, which crystallise from hot water or alcohol in golden-yellow laminæ, scales, or granules. Contains, after drying over oil of vitriol, 31·4 to 31·6 p. c. gold ($C^{32}NH^{19}O^8,HCl,AuCl^3 = 31·28$ p. c. Au.). Melts when heated, and yields a large sublimate of benzoic acid (Niemann).

	At 100°, or over oil of vitriol.			Lossen.
$C^{32}NH^{20}O^8Cl^3$	.... 396·5	.... 80·07	....	
Pt	...... 98·7	...... 19 93	.....	19·48
$C^{32}NH^{19}O^8,HCl,PtCl^2$	... . 495·2	.... 100·00	.. ....	

Acetate of Cocaïne. A solution of cocaïne in alcoholic acetic acid, evaporated over oil of vitriol or in the air, leaves cocaïne free from acetic acid (Lossen).

Oxalate of Cocaïne. — *Mono-acid.* — When a solution of cocaïne in strong alcohol is nearly neutralised with alcoholic (dehydrated) oxalic acid, and anhydrous ether is added thereto until considerable cloudiness is produced, the mixture becomes clear after standing some time, with separation of very fine crystals of the oxalate. These are washed with ether and dried over oil of vitriol. — They do not lose weight at 100°, but melt at a somewhat higher temperature, after which benzoic acid is separated by pouring water upon them (Lossen).

				Lossen.
$C^{32}NH^{19}O^8$	 289	.... 76·25	....	
$C^4H^2O^8$	 90	.... 23·75	.... ..	22·54
$C^{32}NH^{19}O^8,C^4H^2O^8$	 379	.... .. 100 00	....	

Picric acid throws down from hydrochlorate of cocaïne a sulphur-yellow precipitate, which soon cakes together to a resin (Niemann). — *Gallotannic* acid produces, after addition of hydrochloric acid, abundant white flakes, which becomes resinous on standing. — *Cocatannic acid* does not precipitate hydrochlorate of cocaïne (Niemann).

Cocaïne dissolves in *alcohol*, and more easily in *ether* (Niemann).

Ecgonine.

$$C^{18}NH^{15}O^6 = C^{18}NH^{13}O^6,H^2?$$
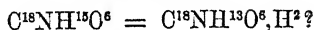
Wöhler & Lossen. *Ann. Pharm.* 121, 371.
Lossen. *Inaugural dissertation.*

From ἐκγονος, a shoot. — *Formation* (p. 302).

Cocaïne is heated to 100° for some hours, with concentrated hydro chloric acid, in a sealed tube. The benzoic acid thereby formed is removed, the last portions by shaking with ether, and the solution of hydrochlorate of ecgonine is freed from excess of hydrochloric acid by evaporation, and from combined acid by agitating its aqueous solution with oxide of silver and filtering. The filtrate is then evaporated and the residue freed from traces of oxide of silver by dissolving it in alcohol. On spontaneous evaporation of the solution, a thick liquid remains, which solidifies in fine needles.

Colourless, inodorous needles, having a bitter-sweet taste. Loses adhering or combined water slowly at 100°.

		at 120°.				Lossen.
18	C	108	....	58·38	....	58·69
	N	14	....	7·57	....	
15	H	15	....	8·11	....	8·32
6	O	48	...	25·94	...	
C¹⁸NH¹⁵O⁶		185	....	100·00	....	

Lossen's formula contains 1 at. hydrogen more   See page 301.

Ecgonine is very easily soluble in *water*. — The *hydrochlorate* forms delicate needles, rather difficultly soluble in cold strong alcohol.

Chloroplatinate of Ecgonine. A mixture of hydrochlorate of ecgo-nine with chloride of platinum and strong alcohol, throws down orange-red prisms which may be washed with alcohol.

		at 100°.				Lossen.
18	C	108·0	....	27·60	....	27·91
	N	14·0	....	3·57	....	
16	H	16·0	....	4·09	....	4·41
6	O	48·0	....	12·27	....	
	Pt	98·7	....	25·23	....	24·80
3	Cl	106·5	....	27·24	....	
C¹⁸NH¹⁵O⁶,HCl,PtCl³		391·2	....	100·00	....	

Ecgonin is more easily soluble in dilute than in absolute *alcohol*; it is insoluble in *ether*.

Appendix to Cocaïne.

Hygrine.

WÖHLER & LOSSEN. *Ann. Pharm.* 121, 374.
LOSSEN. *Dissertation.*

From ὑγρός, *fluid.* — An organic base occurring, together with cocaïne in coca-leaves.

In preparing cocaïne as described on page 300, if to the slightly alka-line liquid from which the cocaine has been extracted by ether, more carbonate of soda is added, and it is then again shaken with ether, it yields hygrine and a neutral oil having an odour of tobacco. These substances remain behind when the ether is distilled; on further heat-

ing the residue till it boils, the temperature quickly rises to above 280°, and a brown alkaline oil distils over, while a black resin is left behind. — When the distillate is maintained at a temperature of 140°, for some hours, in a stream of hydrogen, the greater part passes over of a yellow colour (*a*); while the remainder volatilises only at 140° to 230°, and condenses to a thick brown oil (*b*). Hygrine is contained in both portions; that in *b*, however, is contaminated with a neutral oil; that in *a* with an easily volatilised substance. To remove a little ammonia present, *a* is converted into oxalate, the salt dissolved in absolute alcohol, the solution evaporated, and the residue mixed with caustic potash, which separates the hygrine in the form of oil. The alkaline solution is heated to boiling in a stream of hydrogen, when the hygrine, dissolved in the water, passes over (by adding water to the residue and again distilling to dryness, a further quantity may be obtained), and is extracted from the distillate by ether; on again distilling the ethereal solution, the hygrine remains behind. — The neutral oil in *b* is removed by dissolving *b* in water containing hydrochloric acid, shaking the solution with ether, and separating the ethereal layer; after which, the acid solution is supersaturated with caustic soda, and the hygrine taken up by ether, as in *a* (Lossen).

Properties Thick, pale-yellow oil, having a strong alkaline reaction, a burning taste, and an odour of termethylamine. It produces white clouds with the volatile acids. — Distils very slowly with vapour of water. It does not appear to be poisonous.

Hygrine does not dissolve in *water* in all proportions. The aqueous solution forms a white precipitate with protochloride of tin, yellowish with sulphate of iron, light blue with sulphate of copper; on boiling the solution, the copper precipitate becomes granular, but not brown. Hygrine forms white precipitates with chloride of mercury and nitrate of silver; the silver precipitate quickly turns brown.

Hygrine combines with *hydrochloric acid*, forming deliquescent crystals. The aqueous hydrochlorate forms a brown flocculent precipitate with *biniodide of potassium*, red-white with *protochloride of tin*, white with *corrosive sublimate*, partly flocculent and partly in oily drops. With *bichloride of platinum* it forms dirty white-yellow (or red) flakes, which are decomposed by heating the liquid, and do not appear in very dilute solutions. *Picric acid* throws down from hydrochlorate of hygrine a yellow powder; *gallotannic acid*, a white precipitate.

Hygrine dissolves in *alcohol* and in *ether*.

<center>*Primary Nucleus* $C^{32}H^{28}$.</center>

Linoleic Acid.

$$C^{32}H^{28}O^4 = C^{32}H^{28}O^4.$$
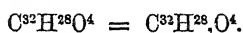
PELOUZE & BOUDET. *Ann. Chim. Phys.* 69, 43.
LAURENT. *Ann. Chim. Phys.* 65, 150 and 298.
LIEBIG. *Ann. Pharm.* 33, 113.
SACC. *Ann. Pharm.* 51, 214.
SCHÜLER. *Ann. Pharm.* 101, 252.

A. C. Oudemanns, Jun. *Scheikund. Verhandel. en Onderzoek.*, 2 Deel.
1 Stuk. *Onzerdoek.* 184 (Rotterdam, 1858).

Papaveroleic acid.   Trockenölsäure. — Occurs in linseed-oil (p. 308)
(Schuler); in poppy-oil (p. 312) (Oudemanns), and perhaps also in the
other drying oils.

Preparation. Linseed oil (or poppy-oil) is saponified, and the soap
purified by repeated salting out, after which it is dissolved in a large
quantity of water, and thrown down by an excess of chloride of
calcium. The precipitated lime-salt is washed, pressed, and digested
in ether, which dissolves out the linoleate of lime, and leaves the salts
of the solid fatty acids undissolved. The ethereal solution is decom-
posed by cold hydrochloric acid, whereby the linoleic acid is separated,
and remains dissolved in the ether; the solution is drawn off, and the
ether distilled at as low a temperature as possible, in a stream of
hydrogen. There then remains dark-yellow linoleic acid, which is
dissolved in alcohol, and precipitated by ammonia and chloride of
barium. The baryta-salt, after being washed and pressed, is dis-
solved in ether, and the warts and granules gradually formed in the
solution, are repeatedly crystallised from ether. From the baryta-
salt, the acid is separated by agitating with ether and hydrochloric
acid, pipetting off the ethereal layer of liquid, and distilling off the
ether; it is dried in a vacuum over oil of vitriol and a mixture of
sulphate of iron and lime (Schüler). A similar method is employed by
Oudemanns, who, however, prefers precipitating the linoleate of soda
by chloride of calcium in a strongly ammoniacal solution. — Sacc digests
linseed-oil with oxide of lead and water, at a gentle heat; exhausts the
pale-grey, greasy soap with ether, which leaves margarate (palmitate
according to Schüler) and a little basic linoleate of lead undissolved;
evaporates the ethereal solution; and decomposes the residue with
hydrochloric acid. The acid thus obtained is washed with boiling water,
dissolved in ether, and recovered by evaporating the solution. Or, he
decomposes the lead-salt with hydrosulphuric acid, and extracts the
linoleic acid with ether.

Properties. Faint-yellow, limpid oil, of sp. gr. 0·9206 at 14°,
having a high refractive power, and a weak acid reaction. Does not
solidify at −18°. Tastes mild at first, afterwards harsh (Schüler).
More limpid than poppy-oil (Oudemanns). Sacc's linoleic acid was between
pale and orange-yellow, limpid, inodorous, and partially oxidised.

						Sacc. *mean.*		Schüler. *mean.*		Oudemanns. *mean.*
32	C	192	....	76·19	....	75·51	....	76 07	....	75·87
28	H	28	...	11·11	....	10·65	....	11·15	....	11·44
4	O	32	....	12 70	....	13·84	..	12 78	....	12·69
C³²H²⁸O⁴		252	....	100·00	....	100·00	....	100·00	....	100·00

Sacc gave the formula C⁴⁶H³⁹O⁶.

Decompositions. 1. On standing in the *air* for ten weeks, the acid
absorbs 2 p. c. oxygen, and becomes viscid and tough (Schüler). It
takes up more oxygen the fresher it is, and thickens, so that at last it

will scarcely flow, but remains colourless, and does not evolve carbonic acid (Oudemanns). A thin layer on wood exposed to the air forms a varnish; on glass it merely becomes tough (Schüler). Linoleate of potash or soda, containing an excess of alkali, exposed in the finely divided state to the air, absorbs oxygen greedily, and becomes yellow and dry; it then dissolves in water with dark brown-red colour, and deposits, on addition of hydrochloric acid, a brown greasy resin, similar to that produced by the action of nitric acid (Sacc). — 2. By *dry distillation*, products are formed, different from those yielded by oleic acid (Laurent). — 3. With *nitric acid*, the acid swells up considerably, and yields a greasy resin, suberic acid, and a little oxalic acid, the last probably derived from adhering ether (Sacc). The resin is lemon-yellow, but becomes dark brown after repeated melting with water; it has an aromatic odour, is strongly reddened by alkalis, and still contains nitric acid. After being saponified with caustic potash, again separated by hydrochloric acid, washed, and dried in the water-bath, it contains 65·10 p. c. C., 9·20 H., and 25·70 O. Concentrated nitric acid slowly converts it into suberic acid (Sacc). — When 1 pt. linoleic acid is heated with 2 pts. nitric acid, a violent reaction ensues, with production of a deep-red, thick, tenacious mass, which, after a while, again becomes limpid. After 24 hours the whole is transformed into a semi-solid mass, containing a fatty acid which melts at 56° (probably already mixed with the linoleic acid Kr.), suberic acid, and a large quantity of oxalic acid, (Bromeis, *Ann. Pharm.* 35, 100) — *Nitrous acid* and *mercurous nitrate* do not form elaïdic acid with linoleic acid (Pelouze & Boudet. Laurent. Schüler. Oudemanns).

Combinations. Insoluble in *water.*

Linoleates. — The mono-acid salts are difficult to obtain pure, and generally contain too small a proportion of base, on account of their easy conversion into acid salts (Schüler; Oudemanns). They are white, for the most part uncrystallisable, and separate from their hot solutions in flakes; by spontaneous evaporation they are obtained in the form of a jelly. When exposed to the air, they become coloured and odorous. They are soluble in alcohol and ether (Oudemanns).

Soda-salt. — When the acid is dissolved in caustic soda, salted out with chloride of sodium, and dried, and the residue is freed from chloride of sodium by dissolving in ether and evaporating the solution, an acid salt is obtained, containing 7·5 p. c. soda, and corresponding to the formula $2(C^{32}H^{27}NaO^4), C^{32}H^{28}O^4$ (Oudemanns), (calc. = 7·75 p. c. NaO).

Baryta-salt. — The salt produced by chloride of barium, with the acid to which a large excess of ammonia has been added, contains a proportion of baryta varying from 12·04 to 24 p. c. ($C^{32}H^{27}BaO^4 = 23·46$ p. c. BaO). — White; separates from alcohol, on cooling, in microscopic crystals, and from ether, by spontaneous evaporation, in more distinct crystals. Exposed to the air, or when kept, and also on boiling with alcohol, it becomes yellow and sticky. Dissolves very easily in ether, less easily in alcohol; insoluble in water (Oudemanns).

Lime-salt. Resembles the baryta-salt. It was only once obtained of the composition following, and mostly contained a smaller proportion of lime (Oudemanns).

				Oudemanns.
32 C	 192	....	70·85	.... 70·04
27 H	 27	....	9·96	.... 10·21
3 O	 24	....	8·85	... ... 10·03
CaO	 28	....	10·34	.... 9·72
C³²H²⁷CaO⁴	 271	....	100·00	.... 100·00

The *Zinc-* and *Magnesia-salts* are insoluble in water. — The *Cupric-salt* is bluish-green, insoluble in water, and nearly so in alcohol (Oudemanns).

Lead-salt. — The acid dissolves a large quantity of oxide of lead, and forms therewith a solid plaster-like mass ; with a smaller quantity of oxide of lead, it forms a thick fluid which, on exposure to the air, remains for a long time greasy, and of the consistence of ointment (Liebig). The ethereal solution of the lead-salt becomes resinised during evaporation, and throws down a white basic salt, upon which an acid, red-brown, jelly-like salt is deposited; this last smells like linseed-oil, and shows a varying composition on analysis. — Exposed to the air in thin layers upon wood, linoleate of lead does not form a varnish, but strips off in scales (Sacc).

Silver-salt. Nitrate of silver throws down from the soda-salt, a white precipitate, which soon blackens from reduction of silver. It dissolves readily in aqueous ammonia, and, on evaporating the solution, a portion crystallises out ; another portion is decomposed and colours the liquid black (Oudemanns).

The acid dissolves easily in *ether*, less easily in *alcohol*.

Appendix to Linoleic Acid.

Drying Oils.

The vegetable oils occurring in nature, which, when exposed to the air in thin layers, dry up to a transparent, resinous, not brittle mass, are also in their other characters distinguished in many ways from the non-drying oils containing olein. It is probable that they contain, as in the case of linseed-oil—the one most accurately investigated in this respect—on the one hand, a glyceride of linoleic acid, which, if isolated, would form the hypothetical dry fat (*Trockenfett*) of the older chemists, and on the other hand, palmitin (together with stearin ?), by the varying proportions of which their differences are determined. In an impure state they contain also mucus, gum, and albumin, as well as a yellow colouring principle possessing taste and smell.

1. *Linseed oil.* The cold-pressed oil of the fresh seeds is of a pale-yellow colour, and without disagreeable taste. The commercial oil is dark-yellow, and has a sharp penetrating smell and taste. Specific gravity at $13° = 0 9347$ (Schüler, Schübler); 0·9337 (van Kerchoff, *Lieb. Kopp. Jahresber.* 1859, 701); other statements vary between 0·928 and 0·953. Sp gr. at $12° = 0.9395$; at $25° = 0.931$; at $50° = 0.9125$; at $94° = 0.8815$, the sp. gr. of water at $15°$ being 1 (Saussure). Does not solidify at $-15°$ to $-16°$ (Gusserow), nor at

— 20° (Brandis); according to Schüler, it deposits a little solid fat at — 18°. — Contains, on an average, 78·11 p. c. C., 10·96 H., and 10·93 O. (Sacc);the cold-drawn oil contains, on an average, 75·17 p. c. C., 10·98 H., and 13·85 O., corresponding to the formula $C^{30}H^{28}O^4$ (Lefort). (See Saussure's analysis, *Ann. Chim. Phys.* 13, 338).

Contains margarin (palmitin, according to Schüler; stearin, according to Unverdorben), and linoleic acid in combination with glycerin (Sacc). By saponification, it yields $\frac{1}{10}$th margarate, and $\frac{69}{10}$ths linoleate of lead (Gusserow, *Kastn. Arch.* 19, 80).

When linseed oil is exposed to sunshine for some weeks, in contact with an aqueous solution of an equal weight of sulphate of iron, it becomes limpid and colourless. Exposed to the air in thin layers, it dries up to a transparent, resinous, moderately elastic mass, resembling caoutchouc; when heated, however, it does not melt, but carbonises and burns (Leucho, *Kastn. Arch.* 3, 107). A peculiar fat is produced at the same time, together with a crumbly substance, insoluble in ether, so that the drying process seems somewhat to resemble the decomposition of axin (see below) (Hoppe, *J. pr. Chem.* 80, 117). Mixed with chalk so as to form a powder, and exposed to the air for four weeks, it dries up completely; and on dissolving out the carbonate of lime with hydrochloric acid, and exhausting the residue with ether, a white mass of the consistence of tar is obtained, which behaves like oleic acid altered by exposure to the air. There remains behind resinous linseed-oil in the form of a yellowish conglomerate mass, which is insoluble in alcohol, ether, volatile and fixed oils, is converted by alcoholic hydrochloric acid into a tarry substance, and dissolves in caustic potash (Unverdorben, *Schw.* 17, 245).

Impure oil, containing mucus or albumin, becomes rancid in the air, more quickly in sunshine, and has then a repulsive odour and taste, a dark colour, and acid reaction. — Concerning the formation of oxonised oxygen in the oxidation of linseed-oil, see Schönbein (*J. pr. Chem.* 74, 338).— When the oil is boiled for some time, till it loses about $\frac{1}{6}$ of its weight, it becomes thicker, tenacious, and viscid, and dries up still more readily than in the fresh state, to a tough, turpentine-like mass, scarcely soluble in oils: *Printers' varnish*.

Linseed-oil (nut- or poppy-oil), heated to about 320°—375°, takes fire and burns quietly, without further heating from without, till tar or charcoal remains. If the burning be interrupted by closing the vessel, there remains a brown, turpentine-like body called *Bird-lime*. When this substance is boiled continuously with water containing nitric acid (water being added so as to prevent the too violent action of the acid), an odour of acrolein is constantly evolved, and the bird-lime becomes solid, of the consistence of plaster, resembles India-rubber, and no longer sticks to the fingers. It is then not completely fusible, dissolves to an emulsion in bisulphide of carbon, shrinks when boiled with concentrated caustic potash, dissolves only on addition of water, and is again precipitated from the solution by acids. This substance is soluble in alcoholic potash and precipitable by acids; it swells in ether free from alcohol, and partly dissolves in a larger quantity of ether; alcohol precipitates it from the solution. In rock-oil it swells without dissolving; also in a little oil of turpentine, but dissolves completely in a larger quantity, and remains unaltered on evaporation. Linseed- and nut-oils yield 8 or 10 times as much of this caoutchouc-like substance as poppy-oil (Jonas, *N. Br. Arch.* 46, 159; *J. pr. Chem.* 37, 381).

Submitted to *dry distillation*, linseed-oil gives off, without boiling, white vapours, which condense to a colourless oil having an odour of bread; on the disappearance of these vapours, it begins to boil, expands, and yields a distillate of brown empyreumatic products, until a mass resembling jelly and caoutchouc remains behind (Sacc.). — It yields by dry distillation the same products as poppy-oil, but less margaric acid (Bussy & Lecanu). See also vii. 242. Hess's supposed aldehyde, obtained by the dry distillation of linseed oil, is acrolein (Redtenbacher, *Ann. Pharm.* 47, 114). *Sulphur* dissolves in hot linseed-oil with red colour, partially crystallising on cooling; on longer heating, the oil takes up, with evolution of hydrosulphuric acid, $\frac{1}{4}$th its weight of sulphur, and forms therewith a brown viscid mass: *fatty balsam of sulphur*. See Radig, Herst & Ulex (*N. Br. Arch.* 2, 15); also Reinsch. (*J. pr. Chem.* 13, 136). On distilling linseed-oil with sulphur, a large quantity of hydrosulphuric acid is evolved, and odmyl (x. 97) is obtained, besides other products (Anderson). Linseed-oil dissolves *selenium* (Berzelius); it dissolves nearly $\frac{1}{16}$ *arsenious acid*, whereby it is rendered heavier, precipitable by oil of vitriol and hydrochloric acid, and coagulable by alkalis (W. Henry, *Schw. J.* 2, 636). — *Phosphorus* becomes scarlet-red by boiling with linseed-oil (Reinsch. *J. pr. Chem.* 14, 257). Heated with $\frac{1}{4}$ its weight of phosphorus to 75°, the oil becomes brown-black, and after cooling is leathery and insoluble in linseed-oil; $\frac{1}{5}$ phosphorus forms a thin tar, which mixes with drying oils (Jonas, *N. Br. Arch.* 70, 139). — When linseed-oil is heated with $\frac{1}{2}$ *iodine*, there pass over, first iodine, then an empyreumatic oil coloured brown by iodine; afterwards white vapours of hydriodic acid are evolved, followed by a thick yellowish oil, and at last charcoal containing iodine remains (Reinsch. *J. pr. Chem.* 14. 263). — *Brominated linseed-oil* is brown (see below), smells like linseed-oil when heated, has a sp. gr. of 1·349 at 14·5°, and contains 40·77 p. c. bromine, corresponding to the formula $C^{30}Br^2H^{26}O^4$. *Chlorinated linseed-oil* is a dark-yellow, thick fluid, of sp. gr. 1·088 at 6·5°, and contains 22·62 p. c. chlorine ($C^3 Cl^2H^{26}O^4$) (Lefort, *N. J. Pharm.* 23, 343). — On mixing from 15 to 25 parts *chloride of sulphur* with 100 parts linseed-oil, caoutchouc-like products are obtained, which are the harder the more chloride of sulphur they contain, and are not attacked by moderately dilute acids and aqueous alkalis, but are ultimately saponified by concentrated alkalis. They become brown at 120°, and blacken and melt at a higher temperature. The addition of 5 p. c. chloride of sulphur thickens linseed-oil, but does not cause it to harden; the product still exhibits to solvents the same relations as the fatty oils. When to a solution of 1 part linseed-oil in 30 or 40 parts bisulphide of carbon, a quantity of chloride of sulphur is added equal to $\frac{1}{4}$th the weight of the oil, the mixture remains fluid for some days, and dries up to a varnish on wood (Perra, *Compt. rend.* 47, 878. — See also *Compt. rend.* 47, 972). — With $\frac{1}{2}$ its volume of syrupy *phosphoric acid*, linseed-oil becomes brownish-yellow or green (Calvert). — Cold *oil of vitriol* colours it yellowish-brown (Gaultier de Claubry), dark red-brown (Heidenreich von Kerckhoff); it coagulates the oil, colours it purple-red, violet, and black, and evolves sulphurous and formic acids; there remains at last a tough, black, ropy, saponifiable mass (Sacc). From this last, water and alcohol take up substances which precipitate gelatin: *Hatchett's artificial tannin*. A mixture of 5 vol. linseed-oil with 1 vol. sulphuric acid of sp. gr. 1·475 to 1·635 shaken vigorously, becomes green in 15 minutes (Calvert). When 15 gr.

linseed-oil are mixed with $7\frac{1}{2}$ gr. sulphuric acid containing 90 p. c. oil of vitriol, the temperature rises to 75° (Fehling *Dingl.* 129, 53). — Linseed-oil takes fire with fuming *nitric acid*. Linseed-, hemp-, and poppy-oils take fire more easily than nut-oil; with dilute nitric acid an addition of sulphuric acid is necessary (Rouelle). A vigorously shaken mixture of linseed-oil with $\frac{1}{2}$ its volume of nitric acid of sp. gr. 1·18 to 1·22, becomes yellow in 5 minutes; with acid of sp. gr. 1·33, green to brown; with nitro-sulphuric (equal parts of oil of vitriol and nitric acid), green (Calvert, *Phil. Mag.* [4] 7, 101; *J. pr. Chem.* 61, 354). — (See also Lescallier, *J. Pharm.* 13, 203). Linseed-oil shaken with water and very dilute nitric acid, is decolorised after some time, and converted into a varnish (*Alm.* 1782, 49). On dropping 2 to 4 drams of strong nitric acid into a hundred-weight of hot linseed-oil, a slimy sediment is formed, with frothing, and the oil is changed to a varnish, as with oxide of lead (Jonas, *Ann. Pharm.* 34, 238). — A mixture of 1 part linseed-oil and 2 parts commercial nitric acid, heated with 4 times its bulk of water, acquires a red colour, swells up, evolves nitric oxide, and forms a tough, elastic resin. This last contains margaric acid, and the mother-liquor oxalic and suberic acids. The resin, heated with nitric acid, again becomes oily, and is then decomposed (the margaric acid only remaining), with formation of suberic and pimelic acids, and a volatile fatty substance having the odour of butyric acid (Sacc). — With *nitrous acid* linseed-oil does not form elaïdic acid (Pelouze & Boudet). In contact with aqueous *ammonia* and alcohol, it is attacked with difficulty, and yields a small quantity of warty crystals of an amide which melts at 100°, solidifies at 97°, and dissolves easily in alcohol; it contains, on an average, 75·25 p. c. C., 13·02 H., and 5·03 N., and has therefore the composition of margaramide, with which it is identical (Rowney, *J. pr. Chem.* 67, 159). — Linseed-oil yields with *alkalis*, a very soft soap. On heating with $\frac{1}{2}$ its volume of caustic soda of sp. gr. 1·34, it turns yellow and remains fluid (Calvert). By distillation with an excess of alkali, it evolves hydrogen, together with a fishy odour, and yields a green distillate (Al. Müller, *Handwörterb.* 6, 874). — *Potassium* and *sodium* oxidise in linseed-oil somewhat more quickly than in volatile oils, with formation of soap (Gay-Lussac & Thénard). Linseed-oil is oxidised with peculiar facility by *bichromate of potash* and dilute sulphuric acid, and yields an acid, strongly smelling distillate (Arzbächer, *Ann. Pharm.* 73, 199). — It dissolves oxide of lead when heated, and is decolorised thereby and rendered more easily drying, forming what is called *boiled oil* (see Liebig, *Ann. Pharm.* 33, 110; W. Henry, *Scher. J.* 2, 636; Schindler, *N. Br. Arch.* 41, 146; Varrentrapp, *Handwörterb.* 3, 123). — When shaken with *basic acetate of lead* and left at rest, it throws down a turbid mucus containing oxide of lead, above which is a yellow varnish containing 4 or 5 p. c. oxide of lead. — Exposed to the sun in contact with *mercuric oxide*, it reduces the mercury to a liquid mass (Fuchs, *Ann. Pharm.* 20, 200); partial reduction takes place in strong sunshine, the oxide becoming blackish-grey; but it is only when heat is applied, that a small quantity of metal is obtained (*Ann. Pharm.* 20, 200).

Linseed-oil shaken with an equal volume of *alcohol* of sp. gr. 0·815, colours it deep greenish-yellow (Davidson, *Edinb. N. Phil. J.* 250; *J. pr. Chem.* 20, 235); it gives up to boiling alcohol of 60 p. c., with partial decoloration, a little acid, resin, and colouring matter. When shaken with absolute alcohol it splits up into tallow, an oily alcohol,

and an alcoholic oil (Leo Mayer, *Berl. Jahrb.* 1827, 1. 118).—It dissolves according to Buchholz, in about 5 parts boiling, and 5 parts cold alcohol ; according to Brandes (*Gilb.* 44, 289) in 32 parts alcohol of sp. gr. 0·82 and 1·6 part ether.

2. *Hemp-oil.*—From the seeds of *Cannabis sativa.* Greenish or brownish yellow at first; yellow after exposure to air and light. Sp. gr. 0·9276 (Schübler), 0·928 at 19° (Trommsdorff), 0·9267 (van Kerckhoff). Smells like hemp and has a mild taste (Buchholz). Contains on an average, 70·97 p. c. C., 11·77 H. and 17·26 (Lefort). *Chlorinated Hemp-oil* is yellowish-brown, of the consistency of honey, and of sp. gr. 1·104 ; it contains 27·35 p. c. chlorine. *Brominated Hemp-oil* is greenish-yellow, of buttery consistence, has a sp. gr. of 1·411 at 16·5, and contains 46·36 p. c. bromine. Lefort gives for the two the formulæ $C^{22}Cl^2H^{20}O^4$ and $C^{22}Br^2H^{20}O^4$.—The oil is coloured green when shaken with ¼th of its volume of syrupy *phosphoric acid*, also, after 15 minutes, when shaken with the same proportion of *sulphuric acid* of sp. gr. 1·475 to 1·635, and in 5 minutes with *nitric acid* of sp. gr. 1·18. Nitric acid of sp. gr. 1·22 to 1·33 colours it greenish dirty-brown ; *nitro-sulphuric* acid black, after ten minutes (Calvert).—Saponifies with difficulty and only after long boiling, yielding a potash-soap almost as soft as that obtained with linseed-oil; the soda-soap separated by salt is also soft (Trommsdorff). Heated with ¼th its bulk of solution of caustic soda of sp. gr. 1·34, it is coloured yellowish-brown, and thickens, so that it does not flow from the inverted vessel (Calvert).—Dissolves in 30 parts of cold, and in all proportions of boiling absolute *alcohol* (Buchholz, *A. Gehl.* 6, 615); a solution in 12 parts hot absolute alcohol deposits stearin in the cold (Trommsdorff, *J. f. techn. Chem* 10, 273. Dissolves completely in *ether*, with green yellowish colour.—See also Resal (*Ann. Chim.* 64, 261); Hess (*Pogg.* 38, 380).

3. *Poppy-oil.* From the seeds of *Papaver somniferum.* Pale-yellow ; limpid ; tastes slightly sharp like nut-oil. Neutral. Sp. gr. 0·9125 (Brandes & Reiche), 0·922 (Brandes), 0·9238 (Brisson), 0·9243 (Schübler), 0·9253 (Lefebore). Does not solidify or become turbid at − 10° to − 12° (Gusserow). Solidifies at − 18° and is not entirely thawed in three hours at − 3° (Brandes). Contains 76·63 p. c. C., 11·63 H., and 11·74 O. (Sacc) ; on the average, 77·2 C., 11·31 H., and 11·49 O. (Lefort). Contains linoleic acid (Oudemanns), probably together with other acids, as glycerides : by saponification, 9·4 p. c. glycerin and 95 p. c. fatty acids are obtained ; the latter are fluid at 24° to 26°, and at 15° become thick, and deposit margaric acid ; from 100 parts of their lead-salts ether takes up 83·3 parts (Gusserow, *Kastn. Arch.* 19, 80). The oil extracted by ether from the seeds of the white poppy does not contain morphine (Meurein, *N. J. Pharm.* 23, 338). Poppy-oil throws down at 200° a deposit of slimy scales, and becomes quite colourless ; soon afterwards it boils, and evolves, with a penetrating odour, carburetted hydrogen and carbonic oxide gases, with which a little carbonic acid is mixed at the commencement only. The first distillate, amounting to ⅓ of the oil, is yellow, has a powerful odour, and congeals at 20° to a soft mass : it is composed of a large quantity of oleic acid. a little margaric, sebacic and acetic acids, acrolein, and empyreumatic oils.—The oil remaining in the retort forms a homogeneous, semi-solid, brown mass, and contains no margaric or oleic acid : when this is again distilled till ⅓ of the whole quantity of

oil has passed over, there is obtained, without any repulsive odour, a pale-green neutral distillate, which remains fluid at $0°$, and turns dark-brown in the air; it possesses a slightly empyreumatic but not irritating odour, is insoluble in caustic potash and but slightly soluble in alcohol.—Lastly, on still further heating, whereby the oil is coloured and carbonised and the bottom of the retort becomes red-hot, yellow vapours arise, consisting probably of chrysene (xv. 1) (Bussy and Lecanu, *J. Pharm.* 11, 361; *Ann. Chim. Phys.* 30, 5).

Poppy-oil oxidises quickly in the *air*, and appears to be more drying than linseed-oil (Sacc). —When it is heated with *bichromate of potash* and sulphuric acid, a solid fat, caproic acid, and a neutral oil possessing the characters of valeric aldehyde distil over; the oil contains $68·54$ C., $11·78$ H., and $19·68$ O. (Arzbächer, *Ann. Pharm.* 73, 200. — Phosphorus dissolves, according to Buchholz, in 36 parts of cold, and 34 parts hot poppy-oil, partially crystallising on cooling; the solution shines in the dark, fumes on admission of air, smells like phosphuretted hydrogen, and evolves that gas when heated; the addition of a little volatile oil prevents the phosphorescence (Kahlert, *Schw.* 47, 366). See Böttger, (*Schw.* 68, 145; Walcker, *Pogg.* 6, 125).—A solution of 1 part phosphorus in 12 parts poppy-oil separates, at $75°$ to $100°$, into a permanently fluid portion and a substance resembling caoutchouc (Jonas, *N. Br. Arch.* 70, 139).—Chlorinated-poppy oil is dark-yellow, of the consistence of castor-oil, of sp. gr. $1·070$ at $3°$, and contains $20·4$ p. c. chlorine, corresponding to the formula $C^{36}Cl^2H^{30}O^4$. Brominated poppy-oil is pale-yellow, of sp. gr. $1·279$ at $2°$, and contains $36·63$ p. c. bromine, agreeing with the formula $C^{36}Br^2H^{30}O^4$ (Lefort). —See also Knop (*Pharm. Centr.* 1854, 321, 403 and 498.)—Triturated with $\frac{1}{8}$ of its weight of *chloride of lime*, it forms a thick soap which does not become clear when left at rest; by agitation with aqueous chloride of lime, it is rendered tenacious, difficultly liquefiable, and sticky. When 10 cub. cent. of *oil of vitriol* are cautiously added to 50 grammes poppy-oil, the temperature rises to $74·5°$, with considerable frothing, from the evolution of a large quantity of sulphurous acid (Maumené, *Compt. rend.* 35, 572). When 15 grammes poppy-oil are mixed with 5 grammes oil of vitriol, the temperature rises to $70°$ (Fehling). Poppy-oil is not coloured by agitation with $\frac{1}{2}$ its bulk of sulphuric acid of sp. gr. $1·475$ to $1·635$, nor by similar treatment with *nitric acid* of sp. gr. $1·18$; nitric acid of sp. gr. $1·22$ colours it yellowish-red; that of sp. gr. 1 33 colours it red (Calvert). With alcoholic *ammonia* it yields, more readily than linseed-oil, warty crystals of an amide, which melts at $103°$ (solidifies at $72°$: Carlet), dissolves easily in alcohol, and has the composition of margaramide. (See below.) (Rowney, *J. pr. Chem.* 67. 160).—Easily saponified, and yields, according to Pelletier, a soft soap; according to Sacc, a very white hard soap, which does not undergo alteration in the air, even when it contains free alkali, and therefore differs probably from the soap obtained from linseed-oil (Sacc. *N. Ann. Chim. Phys.* 27, 482).

Poppy-oil dissolves in about 25 parts cold, and 6 parts hot *alcohol*, and mixes with *ether*.

4. *Walnut-oil.* — From the kernel of *Juglans regia.* Greenish, soon turning pale-yellow. Sp. gr. $0·92$ (Brandis), $0·9227$ (Brisson), $0·926$ (Schübler), $0·9213$ at $12°$, $0·2194$ at $25°$, $0·871$ at $94°$, the sp. gr. of water at $15°$ being 1 (Saussure). Inodorous; tastes mild. Congeals at

— 18° to a solid like lard, soon melting at — 3° (Brades); hardens to a white mass at — 27·5°. Contains 78 p. c. C., 10·57 H. (Saussure, *Ann. Chim. Phys.* 13, 338), on the average 70·67 p. c. C., 11·53 H., and 17·80 O. (Lefort). — Boils above 300° (Saussure). Dries better than linseed-oil. — A stratum of walnut-oil 3 lines in thickness in contact with oxygen over mercury in the shade, absorbed in the first eight months only 3 volumes of oxygen, and in the following ten days (in August) all at once 60 volumes; this rapid absorption decreased gradually, and stopped altogether at the end of October. By that time 145 volumes in all had been absorbed, and 21 volumes of carbonic acid evolved, without formation of water; the oil formed a transparent jelly, which did not produce a greasy stain on paper (Saussure). Walnut-oil behaves towards phosphorus in the same manner as poppy-oil. It forms a yellow *chlorinated oil* of the consistence of honey, of sp. gr. 1·111 at 12°, and containing, according to Lefort, 27·19 p. c. chlorine = $C^{22}Cl^2H^{20}O^4$; and a similarly coloured *brominated oil* of sp. gr. 1·409 at 17·5°, containing 46·8 p. c. bromine = $C^{22}Br^2H^{20}O^4$ (Lefort). The oil, shaken with $\frac{1}{5}$ its bulk of *sulphuric acid* of sp. gr. 1·475 to 1·635, exhibits in a quarter of an hour a brownish or brown colour; when similarly treated with *nitric acid* of sp. gr. 1·18, it is coloured yellow in five minutes; with nitric acid of sp. gr. 1·22 to 1·33, red. Syrupy *phosphoric acid* and *nitro-sulphuric acid* colour it (the latter in two minutes) brown-yellow and dark-brown (Calvert). With alcoholic *ammonia*, it forms a very small quantity of an amide solidifying at 68° (Carlet, *Par. Soc. Bull.* 1859, 1, 73). Yields, like linseed oil, a soft soap.

5. *Grape-seed-oil.* From the seeds of *Vitis vinifera.* The expressed oil of the fresh and washed seeds is colourless or yellow, nearly inodorous, and has a sweetish aromatic taste. Sp. gr. 0·91 (0·9202 Hollandt). It remains fluid at — 6°, but solidifies to a buttery mass at — 11°. Possesses drying properties, and when exposed to the air becomes light-yellow, viscid, and rancid (poisonous, according to Hollandt). When saponified, it forms a yellow-grey, very soft soap, which, by distillation with phosphoric acid, yields volatile acids. By digestion with oxide of lead, it forms a varnish. It is insoluble in cold, easily soluble in hot absolute alcohol; soluble in all proportions in ether (J. Fontenelle, *J. Chim. méd.* 3, 66; Schweinsberg, *Mag. Pharm.* 22, 159; Landerer, *Repert.* 67, 108, Hollandt, *Pharm. Viertelj.* 1, 195).

6. *Oil of Deadly Nightshade-seed.* From *Atropa Belladonna.* Sp. gr. 0·925; rather thicker than linseed-oil; becomes very thick and turbid at — 16°, and solidifies at — 27·5°. Inodorous; tastes mild; is not poisonous. Dries slowly (Schübler). Yellow; has a faint odour, like rape-oil; drying (Becher & Buchner, *Repert.* 17, 88).

7. *Oil of Tobacco-seed.* — From *Nicotiana Tabacum.* Pale greenish-yellow, of sp. gr. 0·9232. Nearly as thin as hemp-oil, and perfectly fluid at — 15°. Inodorous, of mild taste (Schübler).

8. *Oil of Henbane-seed.* — From *Hyoscyamus niger.* Sp. gr. 0·913 (Brandis); colourless, moderately fluid. Inodorous; tastes mild. Not completely soluble in 60 parts cold absolute alcohol; abundantly soluble in ether (Brandis, *N. Tr.* 5, 1, 40). Whether or not it is a drying oil is not exactly known.

9. *Sunflower-oil.* — From the seeds of *Helianthus annuus.* Pale-yellow, of sp. gr. 0·9262. Thicker than hemp-oil, thinner than poppy-oil. Solidifies at − 16° to a white-yellow mass. Dries slowly (Schübler).

10. *Oil from the seeds of Hesperis matronalis.* — Greenish, becoming brown in time. Sp. gr. 0·9282. Perfectly fluid at − 15°, nearly inodorous; dries easily (Schübler).

Oil of Gold-of-Pleasure-seed.—From the seed of *Myagrum sativum,* L. *Camelina sativa.* Dec. Pale-yellow, of sp. gr. 0·9252 (Schübler), 0·9282 (Lefebvre), 0·9234 (van Kerchoff). Thicker than hemp-oil; becomes very viscid at − 15°, and solidifies at − 19° to a white butter. Nearly inodorous and tasteless (Schübler).—According to Henry (*J. Pharm.* 16, 71), it is yellow, has a powerful odour and taste, does not solidify at − 6°, but congeals at a lower temperature, and is not a drying oil. Contains a little hydrosulphocyanate of sinapine; yields a soft soap.

12. *Cress-seed-oil.* From *Lepidium sativum.* Brown-yellow; of sp. gr. 0·924; thickens and becomes turbid at − 6° to − 10°, and congeals at −15° to a yellow mass. Has a peculiar smell and taste. Dries slowly (Schübler).

13. *Gourd-seed-oil.* From *Curcubita Pepo.* Pale-yellow, of sp. gr. 0·9231; the most viscid of oils, next to castor- and olive-oils. Solidifies to a grey-yellow mass at −15°. Inodorous, tasteless; dries slowly (Schübler).

14. *Oil of Madia sativa.* Deep-yellow, viscid. Sp. gr. 0·935 at 15°, after purification, 0·9286. Solidifies, according to Winckler, at −10° to −17°; according to Riegel at −22·5. Absorbs, in five months, 150 times its bulk of oxygen, and becomes more viscid. By exposure to the air in a thin layer for six months, it is transformed into a tough white mass. Nitric oxide colours the oil brown-red; when the action is continued for a long time, and the oil is afterwards exposed to the air, it becomes nearly colourless. By digestion for a longer time with oxide of lead, it becomes almost colourless, thickens and resembles Venice turpentine (Riegel, *Jahrb. pr. Pharm.* 4, 345). Yields, by saponification, a solid acid melting at 60°, probably palmitic acid, and a liquid acid which resembles oleic acid, but appears at the same time to be drying; the latter, is perhaps, a mixture, it contains 76·0 p. c. C., 11 H., and 13 O. (Boussingault, *Compt. rend.* 14, 361). The oil from *Madia sativa* (the same which Riegel and Boussingault investigated? Kr.) yields, by saponification, no volatile acid, but traces of an acid the lead-salt of which is soluble in ether, and a solid acid melting at 54° to 55°, and solidifying to a lamellar crystalline mass at 52°. This last is $C^{32}H^{31}O^4$; it contains, on the average, 75·6 p. c. C., 12·56 H., and 11·84 O., and in the silver-salt, 52·76 C., 8·30 H., 32·14 AgO., and 6·80 O. (Luck, *Ann. Pharm.* 54, 124). Luck's acid is a mixture of stearic and palmitic acids, perhaps with a third acid (Heintz, *Pogg.* 92, 600).

15. *Woad-seed-oil.* From *Reseda luteola.* Dark-green, of sp. gr. 0·9358, particularly mobile, even at −15°. Has a repulsive odour and taste. Dries easily (Schübler).

16. *Oil of Scotch Fir-seed.* From *Pinus sylvestris,* L. Brown-yellow,

of sp. gr. 0·9312 ; becomes thicker at —16°, milky at —27·5°, and solid at —30°. Has a faint odour like that of turpentine. Dries easily (Schübler).

17. *Oil of Spruce Fir.* From the seeds of *Abies excelsa*, Dec. ; *Pinus Abies*, L. Sp. gr. 0·9288; yellow, remaining fluid at 15°. Has an after-taste of turpentine (Schübler.).

18. *Oil of Silver Fir-cones.* From *Abies Picea*, Dec. *Pinus Picca*, L. Obtained by expressing the riper seeds. Brown-yellow, of sp. gr. 0·926. Has an agreeable balsamic odour of fir; tastes mild and aromatic, and afterwards produces a slight burning sensation in the palate. It is a mixture of the resin and volatile oil of the seed-capsule with the fatty oil of the albumen ; the latter dries slowly, but is more soluble in absolute alcohol than other drying oils (Zeller, *Repert.* 65, 301; *N. Br. Arch.* 3, 294).

19. *Fatty oil of Spruce Fir.* — Expressed from the fruit. Limpid, scentless, of sp. gr. 0·904. Does not dry up, even when spread in a thin layer. Nitrous gas renders it moderately solid and crystalline, and somewhat yellowish. Dissolves slightly in absolute alcohol, but only at the boiling heat; in 3 vol. cold absolute *ether* (Wurzer, *Repert.* 49, 234).

Brominated and Chlorinated Oils.

LEFORT. *N. J. Pharm.* 23, 278 and 342 ; abstr. *Compt. rend.* 35, 734. *Instit.* 1852, 370 ; *J. pr. Chem.* 58, 139.

When fatty oils are brought in contact with bromine or chlorine, they become hot, give off hydrochloric acid, and yield products in which part of the hydrogen is replaced by an equivalent quantity of bromine or chlorine. Lefort regards these products as probably definite chemical compounds, and assigns to them formulæ which are inconsistent with the fact that many fatty oils deposit solid fats when cooled, and that they may be resolved into glycerin and a number of different fatty acids.

Preparation of Brominated and Chlorinated Oils. The oil is drenched with 8 or 10 pts. of water, heated to between 50° and 80°, and chlorine gas is passed into the liquid as long as it continues to be absorbed. When bromine is used, the water is kept cold at first, and warmed only towards the end of the operation ; the bromine is added by drops as long as its colour disappears, and the excess of bromine is removed, if necessary, by further addition of oil. — The product is washed with warm water, and dissolved in ether ; the solution is shaken up with warm water, and the oil thus freed from acid, is dried at 120°.

The brominated and chlorinated oils are of dark-yellow colour, heavier than water, more viscid than the original oils, and differ from them in taste and odour. — They thicken when exposed to the air, and turn slightly brown at 150°. They boil between 200° and 210°, acquiring a dark-brown colour, but without evolution of chlorine or bromine. They may be kept in closed vessels for a long

time without turning rancid or sour. (For the properties of these products, *see* the several oils.)

Primary Nucleus $C^{32}H^{30}$.

Physetoleic Acid.

$$C^{32}H^{30}O^4 = C^{32}H^{30},O^4.$$
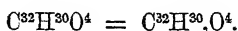
P. G. Hofstädter. *Wien Akad. Ber.* 12, 765; *Ann. Pharm.* 91, 177; *Chem. Centr.* 1854, 808; *Chem. Gaz.* 1844, 465.

Gössmann & Scheven. *Ann. Pharm.* 94, 230; abstr. *J. pr. Chem.* 66, 83; *Pharm. Centr.* 1855, 568; *Chem. Soc Qu. J.* 8, 279; *N. Ann. Chim. Phys.* 46, 230.

Caldwell & Gössmann. *Ann. Pharm.* 99, 305; abstr. *J. pr. Chem.* 70, 79; *Chem. Centr.* 1856, 892; *N. Ann. Chim. Phys.* 49, 111.

F. Hoppe. *J. pr. Chem.* 80, 112; abstr. *Chem. Centr.* 1860, 625; *Rép. Chim. pure*, 3, 158.

Hypogæic acid. — Discovered by Hofstädter in sperm-oil; by Gössmann & Scheven in the oil of *Arachis hypogœa* (*Handb.* viii. *Phytochem.* 8); Caldwell & Gossmann are of opinion that the identity of the acids from these two sources is not satisfactorily proved.

When Hoppe's *axinic acid* $C^{36}H^{28}O^4$, is rapidly oxidised, there is produced — together with aginin, which is insoluble in ether — an acid which may be dissolved out by ether, and crystallises on cooling from a hot saturated alcoholic solution. It forms bulky crystalline laminæ, which shrink on the filter to a film having a silky lustre, melt easily to a light yellow oil, solidify at 35°, and contain on the average, 75·48 p. c. C. and 11·81 H. This acid, when exposed to the air in a melted state, decomposes with rancid odour and separation of brown resinous flakes, and dissolves easily in aqueous alkalis; its baryta-salt contains 60·21 p. c. C., 9·39 H., and 20·63 BaO; the silver-salt at 15° contains 31·42 p. c. silver (calc. 29·91 p. c. Ag.). Hoppe regards it as identical with Gossmann's physetoleic acid. A glyceride of this acid (containing 2 at. glycerin + 3 at. acid – 4 at. water), with 72·8 – 73 12 p. c. C. and 10·87 to 10·90 H., is produced in the oxidation of axin-fat (Hoppe.)

Preparation. 1. *From Earthnut-oil.* The fatty acids of the oil are dissolved in alcohol; arachidic and palmitic acids are precipitated by ammonia and acetate of magnesia; the precipitate is removed; and the filtrate is mixed with ammonia and an alcoholic solution of neutral acetate of lead. The precipitate is collected after a few days, pressed, and dissolved in ether; the ethereal solution is agitated with aqueous hydrochloric acid; the chloride of lead is filtered off; the filtrate is shaken up with water which has been freed from air by boiling; the ethereal layer which separates again on leaving the liquid at rest is taken off; and the ether is removed by distillation. The remaining liquid on cooling deposits yellowish crystals, which may be purified by pressure, and recrystallisation from alcohol at a very low temperature. An additional quantity of crystals may be obtained from the mother-liquor (Gössmann & Scheven).

2. *From Sperm-oil.* The soap prepared by boiling the oil with potash-ley and purified by salting out, is dissolved in boiling alcohol; and the filtrate, after being freed from alcohol by distillation, is diluted

with water, and precipitated with ammoniacal sugar-of-lead.   The precipitate, washed by decantation and dried in the air, is drenched with ether, which dissolves physetoleate of lead, ethal, and undecomposed spermaceti, leaving undissolved the lead-salts of the solid fatty acids. The solution is separated; part of the ether is distilled off ; the residue decomposed by hydrochloric acid ; the ethereal solution mixed with ammoniacal chloride of barium ; the precipitate collected, washed, and dried in a vacuum ; and the ethal and spermaceti are removed from it by cold ether.   On boiling the undissolved physetoleate of baryta repeatedly with alcohol of 93 per cent., and cooling the resulting solutions separately, the portion taken up is deposited as a white powder, which must be collected out of contact with the air, washed with alcohol, and immediately dried in a vacuum.   It may be obtained pure by recrystallising it twice more in the same way, and decomposed by boiling with aqueous tartaric acid (Hofstädter).

Properties.   Colourless, inodorous needles, grouped in stars, melting at 34° to 35° (Gössmann & Scheven), at 30° (Hofstädter), and solidifying at 28° (Hofstädter).

		at 100°.			Gössmann & Scheven. mean.
32 C	.....	192	....	75·59	.... 75·56
30 H	.....	30	....	11·81	.... 11·77
4 O	.....	32	....	12·60	.... 12·67
C^{32}H^{30}O^4	.....	254	....	100·00	.... 100·00

Homologous with cimicic acid (p. 284) and oleic acid (C^{36}H^{34}O^4).

Decompositions.   1. Physetoleic acid, when exposed to the *air*, acquires a yellowish colour, and rancid odour, and then crystallises with difficulty, even at very low temperatures (Gössmann & Scheven). At 100° in an air-bath it turns yellow, acquires the odour of train-oil, and its melting point is lowered to 26·5° (Hofstädter).—2. When subjected to dry distillation, it first gives off a reddish yellow liquid, then yellowish white crystalline sebacic acid (xiv, 493), and lastly, a fetid oil, leaving a small quantity of charcoal (Caldwell & Gössmann).   Hofstadter, who distilled only small quantities of physetoleic acid, did not obtain any sebacic acid. — Physetoleic acid altered by exposure to the air yields less sebacic, and likewise less gaeïdinic acid than the pure acid (Caldwell & Gössmann). — 3. With *nitrous acid* it forms gaeïdinic acid (p. 319) (Caldwell & Gössmann).   This transformation also was not perceptible with Hoffstadter's acid.

Combinations.   The acid is easily saponifiable.

Baryta-salt.   Preparation (see above).— From the alcoholic solution of the acid mixed with excess of ammonia, alcoholic acetate of baryta throws down white granules, which dissolve when heated, and separate again on cooling (Gössmann & Scheven).

		In vacuo.		Hofstadter.		mean.		Gössmann & Scheven.
32 C	.....	192·0	.....	59·72	.....	59·78	.....	
29 H	.....	29·0	.....	9·02	.....	9·26	.....	
3 O	.....	24·0	.....	7·47	.....	7·16	.....	
BaO	.....	76·5	.....	23·79	.....	23·80	.....	24·07
C^{32}H^{29}BaO^4	....	321·5	.....	100·00	.....	100·00	.....	

Copper-salt. — An alcoholic solution of acetate of copper, added to an alcoholic solution of the acid mixed with ammonia, throws down, on cooling, bright blue crystalline grains which do not alter in drying. They sinter together at 75° to a translucent wax; they are easily soluble in alcohol (Gössman & Scheven).

		at 100°.			Gössmann & Scheven.
32	C	192	....	67·37	.... 67·27
29	H	29	....	10·18	.... 10·39
3	O	24	....	8·42	....
	CuO	40	....	14·03	....
$C^{32}H^{29}CuO^4$		285	....	100·00	....

Physetoleic acid dissolves readily in *alcohol* and in *ether*.

Physetoleate of Ethyl.

$$C^{36}H^{34}O^4 = C^4H^5O,C^{32}H^{29}O^3.$$
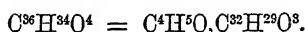
GÖSSMANN & SCHEVEN. *Ann. Pharm.* 94, 234.

Hypogæate of ethyl. Physetoleic or *Hypogæic ether. Physetolvinester.*

A solution of physetoleic acid in alcohol of 95 p. c. repeatedly saturated with hydrochloric acid gas and warmed, deposits this ether, which may be freed from adhering hydrochloric acid by washing with water, from unaltered physetoleic acid by washing with small quantities of alcohol, and dried in a stream of carbonic acid between 100° and 120°.

Yellow, scentless oil, lighter than water, but sinking in alcohol. Not volatile without decomposition. Very slightly soluble in alcohol.

					Gössmann & Scheven.
					mean.
36	C	316	....	76·59	.... 76·73
34	H	34	....	12·05	.... 11·95
4	O	32	....	11·36	.... 11·32
$C^4H^5O,C^{32}H^{29}O^3$		282	....	100·00	.... 100·00

Gaeïdinic Acid.

$$C^{32}H^{30}O^4 = C^{32}H^{30}O^4.$$
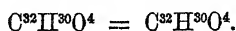
CALDWELL & GÖSSMANN. *Ann. Pharm.* 99, 307; abstr. *J. pr. Chem.* 70, 79; *Chem. Centr.* 1856, 892; *N. Ann. Chim. Phys.* 49, 111; *Lieb. Kopp. Jahresber.* 1856, 494.

Nitrous acid gas is passed into physetoleic acid, as long as the mass becomes more solid; the product is then pressed and repeatedly crystallised from alcohol, till the melting point no longer rises.

Colourless crystalline mass, which melts at 38°, solidifies to a radio-crystalline mass on cooling, and volatilises unaltered at a higher temperature.

				Caldwell & Gössmann.		
						mean.
32 C	....	192	....	75·59	....	75·46
30 H	....	30	....	11·81	....	11·97
4 O	....	32	....	12·60	....	12·57
$C^{32}H^{30}O^4$	....	254	....	100·00	....	100·00

Isomeric with physetoleic acid, to which it is related in the same manner as elaïdic to oleic acid.

Insoluble in *water*.

Gaeïdinate of Soda. — The acid is dissolved in aqueous carbonate of soda, the solution is evaporated, and the salt dissolved out with absolute alcohol, whereby a solution is obtained, which solidifies to a translucent jelly on cooling. Dilute solutions yield crystalline laminæ.

Gaeïdinate of Copper. — From the aqueous soda-salt, sulphate of copper throws down a small quantity of a crystalline precipitate, which dissolves with difficulty in alcohol, and separates therefrom in grains. Melts without decomposition somewhat above 120°.

				Caldwell & Gössmann.		
32 C	....	192	....	67·37	....	67·24
29 H	....	29	....	10·18	....	10 27
3 O	....	24	....	8·42	....	8·66
CuO	....	40	....	14·03	....	13·83
$C^{32}H^{29}CuO^4$	....	285	....	100·00	....	100 00

Gaeïdinate of Silver. — Obtained from the soda-salt by precipitation with nitrate of silver. — White, amorphous powder, which blackens when washed, and especially when heated with water, alcohol, or ether, but does not dissolve.

Gaeïdinic acid dissolves readily in *alcohol* and in *ether*.

Gaeïdinate of Ethyl.

$$C^{36}H^{34}O^4 = C^4H^5O, C^{32}H^{29}O^3.$$
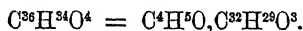
CALDWELL & GÖSSMANN. *Ann. Pharm.* 99, 310.

Gaeïdinic ether.

Hydrochloric acid is passed into a solution absolute alcohol; water is added after 12 hours; gaeïdinic ether and free gaeïdinic acid thereby 1 subjected to the same treatment. The product is v 100° in a stream of hydrogen.

Laminar, crystalline, colourless mass, which me. distils without alteration at a higher temperature. than water, heavier than alcohol.

Caldwell & Gössmann.

36 C	....	216	....	76·59	....	76 37
34 H	....	34	.. ..	12·05	....	12·19
4 O	... ...	32	....	11·36	....	11·44

$C^4H^5O, C^{32}H^{29}O^3$ .... 282 .... 100·00 .... 100·00

Dissolves with difficulty in *alcohol*.

Appendix to Physetoleic Acid.

Fish Oils.

1. *Sperm-oil.* — Occurs, together with spermaceti—from which it is separated by mechanical means—in certain cerebral cavities of the *Physeter macrocephalus.*

When freed as complete¹ as possible from admixed spermaceti-fat, by leaving the latter t ᵒ crystallise out, it is neutral, remains liquid at 18°, is saponified with difficulty by potash, and yields by that process the same fatty acids as spermaceti-fat, but instead of ethal, a neutral product melting at 20° (Chevreul, *Recherches*, 237). Sperm-oil appears to be isomeric with spermaceti-fat or cetin (p. 347) (Stenhouse).— The oil which runs off from the spermaceti-fat solidifies almost completely at 0°, to a compac tlight-brown mass, in consequence of still retaining spermaceti-fat. When saponified, it gives off ammonia, with traces of methylamine, and yields physetoleic acid (p. 317), valerianic acid, small quantities of solid fatty acids, and a small quantity of glycerin (Hofstädter).

On evaporating the mother-liquors obtained in recrystallising ethal from alcohol (see below), an additional quantity of ethal crystallises out at first, and more fatty acids may be precipitated by acetate of baryta, after neutralisation with ammonia. Ultimately, when as great a quantity as possible of ethal has been removed by evaporating, crystallising out, and cooling, any baryta- and ammonia-salt remaining in the liquid by boiling with hydrochloric acid, and the rest of the fatty acids by potash-ley, there remains an oil which does not solidify in the crystalline form at 10° or 12°, volatilises slowly in white vapours at 100°, and passes over, partly decomposed, at a higher temperature. This oil contains, on the average, 76·0 p. c. C., 12·82 H., and 11·18 O., therefore equal numbers of atoms of carbon and hydrogen; but it is still impure (Heintz). From the fatty acids of spermaceti Heintz likewise separated another buttery fat, containing 74·17 p. c. C., 11·63 H., and 14·20 O.

2. *Whale-* or *Train-oil.* — From the blubber of *Balæna misticetus* and other kinds of whale. A train-oil of sp. gr. 0·927 at 20° examined by Chevreul, was brownish, deposited solid fat at a temperature above 0°, and contained olein, margarin, and a small quantity of dolphin-fat (valerin). ᵘ°ⁿᵗⁱᵘᵉᵈ heating to 182°, whale-oil is blackened, and suffers furth⸗ᵗᵉʳ ᶜᶜ n (Bostock, *Thoms. Ann.* 17, 46). Oil of vitriol colours it reddish y⸗ w. With aqueous mercurous nitrate, it forms a yellow salt, which turns brown in a few hours (Lescallier). With alkalis it forms a soft soap. Dissolves arsenious acid and oxide of lead. Sp. gr. 0·924 at 15° (Lefebvre), of South Sea whale-oil 0 9195 ; of that from the Faroe Islands, 0·9293 at 11° (Scharling).

The oil separated from the solid fat by cooling to 0° and filtration, is free from acid reaction, and dissolves at 75° in 0·82 pt. alcohol of sp. 0·795, the solution not becoming turbid at 63°.   With hydrate of potash it quickly forms a brown soap, soluble in water, and containing valeric, oleic, and margaric acids, and a brown colouring matter ; the glycerin separated at the same time is brown, and has an agreeable taste. — The solid fat deposited by cooling the oil, when purified as completely as possible by solution in hot alcohol and cooling, solidifies after fusion, between 21° and 27°. Dissolves in 1·8 pts. hot alcohol of sp. gr. 0·795, and partly crystallises therefrom in white needles.   By saponification it yields margaric and oleic acids, a trace of valerianic acid, 7 p. c. glycerin, and 4 p. c. of a brown substance, which does not melt at 100° C., burns without residue, and dissolves completely in boiling alcohol (Chevreul, *Ann. Chim. Phys.* 7, 373 ; also *Recherches,* 297).

Stinking train-oil may be deodorised by passing steam heated to 160° through it, and will remain sweet for several months (Scharling, *J. pr. Chem.* 50, 377). — Train-oil is immediately blackened by *chlorine* (Chateau, *Mulh. Soc. Bull.* 31, 416). — When 5 vol. whale-oil are heated to boiling with 1 vol. soda-ley of sp. gr. 1·34, a red liquid is formed.   When shaken with sulphuric acid of sp. gr. 1·475, in the proportion of 5 vol. oil to 1 vol. acid, it becomes faintly red after 15 minutes, darker with acid of sp. gr. 1·53, and dark-brown with acid of sp. gr. 1·635. Nitric acid of sp. gr. 1·18 to 1·22, used in like manner instead of the sulphuric acid, colours the oil light yellow in five minutes ; nitric acid of sp. gr. 1·33 colours it red ; syrupy phosphoric acid (only when heated, according to Chateau), colours it dark-red (Calvert, *J. pr. Chem.* 61, 354). — With alcoholic ammonia, whale-oil forms a larger quantity of an amide solidifying at 85° (Carlet, *Par. Soc. Bull.* 1, 73).

3. *Seal-oil.   Seehundsthran. Robbenthran.* — Viscid, frequently dark brown, with a most intolerable odour (Davidson, *Ed. J. of Sc.* 7, 97). Sp. gr. of the light oil 0·9317, of the dark-coloured 0·9303 at 11° (Scharling).   With soda-ley, phosphoric acid, sulphuric acid, and nitric acid of sp. gr. 1·33, it exhibits the same colours as whale-oil, but is reddened likewise by nitric acid of sp. gr. 1·18 and 1·22 (Calvert). With alcoholic ammonia it forms a large quantity of oleamide, melting at 82° (Rowney, *J. pr. Chem.* 67, 160).

4. *Shark-oil.   Haifischthran.*—From *Squalus maximus.* Has a faint yellow colour, a sp. gr. of 0·870 to 0·876, and a repulsive odour. Does not solidify at a few degrees below 0°. Contains 82·77 p. c. C., 12·96 H., and a large quantity of iodine. By dry distillation it yields a yellow oil, having the odour of acrolein, but no sebacic acid. It appears to contain a peculiar oleic acid (Ronalds, *Chem. Gaz.* 1852, 420 ; *J. pr. Chem.* 57, 478).

5. *Sea-calf oil.   Seekalbsthran.*—Thinner than whale, pale brown, transparent, of sp. gr. 1·926 at 11° (Scharling); when boiled with dilute sulphuric acid, it gradually forms a precipitate (Davidson). — The fat of *Salmo Thymailus* is yellow, mild, and has a faint fishy odour. — *Toulourou* oil, from *Pagurus Latro,* is brownish yellow, and mostly rancid.

6. *Pilchard-oil*   Probably from *Clupea Pilchardus.*   Yellowish,

clear, like light-coloured cod-liver oil; smells like train-oil. Contains olein, with a small quantity of resin, a volatile acid resembling valerianic acid, and iodine (Brandes, *N. Br. Arch.* 16, 85).

7. *Porpoise-oil. Meerschweinthran.*—From *Delphinus Phocena.* Obtained by heating the belly-blubber with water. Sp. gr. 0·937 at 16° ; pale yellow; does not redden litmus. Loses its odour, which resembles that of fresh sardines, on exposure to air and light, becoming at the same time darker in colour, then nearly colourless, and acquiring an acid reaction, from liberation of valerianic acid. Consists of olein, not solidifying till cooled to − 15°, margarin, and valerin (xi, 77) (Chevreul). This valerin is identical with that which is produced by heating valerianic acid with glycerin (Berthelot, *N. Ann. Chim. Phys.* 41, 253 ; *Chim. organ.* 2, 87), 100 pts. of the oil yield 16 pts. valerate of baryta, 14 glycerin, 82·2 margaric and oleic acids. With 5 pts. boiling alcohol of sp. gr. 0·821, the oil forms a solution, which becomes turbid as soon as it is removed from the fire; with 1 pt. of alcohol a more stable solution is formed, capable of taking up any further quantity of the oil. On mixing the alcoholic solution with water and distilling, the water retains in solution a small quantity of valerianic acid, a substance having a fishy odour, and a yellow colouring matter (Chevreul, *Recherches*, 287).

8. *Dolphin oil. Delphinthran.*—From *Delphinus globiceps.* Pale yellow; of sp. gr. 0·918 at 20° ; does not redden litmus. Contains cetin. valerin, olein, odoriferous substances, and a yellow colouring matter. —It deposits crystals of cetin at + 5° and again at − 3° ; the remaining oil of sp. gr. 0·924, is yellow, and solidifies at 15° to a soft mass, which becomes perfectly fluid at 20°. — 100 parts of the crude oil yield by saponification, valerianic acid, 12·6 p. c. of brown-yellow glycerin, and 66·8 p. c. of a mixture of margaric acid, oleic acid, and ethal.—100 pts. of the oil freed from cetin yield 34·6 pts. valerate of baryta, 15 pts. glycerin together with odoriferous and colouring matter, 51·7 pts. margaric and oleic acid, and 14·3 pts. ethal mixed with a second neutral substance melting at 27°. — 100 pts. alcohol of sp. gr. 0·812 dissolve at 70°, 100 pts. of dolphin oil, forming a solution which becomes turbid at 52° ; 100 pts. alcohol of sp. gr. 0·795 dissolve at 20°, 123 pts. of the crude oil ; of the oil freed from cetin by cooling, 100 pts. boiling alcohol of specific gravity 0·82, dissolve 149·4 pts. forming a solution which reddens litmus, the red colour disappearing however on addition of water (Chevreul, *Ann. Chim. Phys.* 7, 264; 22, 374: *Recherches*, 291.)

9. *Cod-liver oil. Leberthran   Stockfischthran. Huile de foie de morue, Oleum jecoris Aselli*—Obtained from the livers of various species of *Gadus,* especially from the dorse (*Gadus Cellarius*), the coal-fish (*Gadus Carbonarius*) and the Haakjerius or Hayfisch of Norway (*Gadus Pollachius*) (De Jongh). ¶ The oil recognised by the pharmacopœias is that obtained from the common cod (*Gadus Morrhua,* formerly cal'e l *Asellus major*), and the ling (*G. Molva* or *Lota Molva*): it is received from Newfoundland. England was formerly supplied with the oil from Bergen, obtained from the livers of the dorse and coal-fish. From this source Germany and the North of Europe still receive their supply. Cod-liver oil is prepared on a small scale in the Shetland isles and on the English coast, chiefly from the common cod, the ling and the burbot (*Lota vulgaris*). (*Pereira's Materia Medica,* 4th Ed. 1857, 2 [2],

779) ¶. — When the livers of the fishes are exposed to the sun, light-coloured oil flows out at first, but after a week or a fortnight, putrefaction sets in, and brown oil is obtained (Marder). — *a. Brown Cod-liver oil.* Dark brown, greenish by transmitted light, transparent in thin layers. Sp. gr. 0·929 at 17·5° (De Jongh), 0·928 at 15·5° (Marder); has a peculiar odour, disagreeably empyreumatic and bitter, produces irritation in the throat, and reddens litmus slightly (De Jongh). Does not deposit any solid fat at − 13° (Marder). Soluble in 17 to 20 pts. cold or hot absolute alcohol (De Jongh). Dissolves at 71° in 1 pt. alcohol of 0·846, forming a solution which becomes turbid at 62° and deposits the oil at 48° (Marder). — *b. Paler brown.*—Of the colour of Malaga wine. Sp. gr. 0·924; has a peculiar, not unpleasant odour, fishy taste, producing irritation in the throat, and reddens litmus strongly. Soluble in 31 to 36 pts. of water and 13 pts. of boiling absolute alcohol (De Jongh).

c. Paler and clearer. Of golden-yellow colour, sp. gr. 0·923 at 17·5° (De Jongh), 0·928 at 15·5° (Marder); reacts and tastes like *b*, but less strongly. Deposits a white fat at − 13° (Marder). Soluble in 40 pts. cold and in 22 to 30 pts. boiling absolute alcohol (De Jongh, *L'huile de foi de morue envisagée sous tous les rapports, comme moyen thérapeutique.* Paris, 1853. *Scheik. Onderzoek vierde Stuck,* 336; abstr. *Ann. Pharm.* 48, 362.)— Oil of dorse-liver has a sp. gr. of 0·9313 at 11° (Scharling).

Cod-liver oil consists chiefly of olein and margarin, with smaller quantities of free butyric acid, acetic acid, constituents of the bile, gaduin, and other peculiar substances, about 1 p. c. of salts, and a small quantity of free phosphorus (De Jongh). It contains iodine, bromine, phosphorus, and sulphur (see below). As volatile acids, Wagner found butyric and capric acids; from turbid cod-liver oil, Luck's gadinic acid was deposited. See analyses of cod-liver oil by Marder (*N. Br. Arch.* 13, 153), De Jongh (*Ann. Pharm.* 48, 362), Riegel (*N. Br. Arch.* 70, 23); for Winklers's views respecting the oil, see *J. pr. Pharm.* 25, 140.

When cod-liver oil is shaken up with water, the water takes up a free acid, a resin which separates on evaporation, and substances precipitable by tincture of galls (Marder). Boiling water dissolves from brown cod-liver oil 1·26 p. c., from the clear oil 0·6 p. c. extract, to be further decomposed by successive treatment with ether, absolute alcohol, and aqueous alcohol. the ether taking up biliary acids, the absolute alcohol, colouring matters of the bile, and the aqueous alcohol of 30° B. a black shining substance which dissolves in alkalis, oil of vitriol, and hot acetic acid, and when dissolved in alcohol, forms brown precipitates with baryta-water and neutral acetate of lead. The portion of the aqueous extract of the oil remaining undissolved after this treatment, still contains organic matter, together with salts which are free from potash and iodine (De Jongh).

Phosphorus and sulphur exist in cod-liver oil in the state of organic combination (Gobley, *N. J. Pharm.* 6, 25). Iodine occurs according to Herber (*Ann. Pharm.* 31, 94), De Jongh and others, in all true cod-liver oil; according to Chevallier and Donovan (*J. Chim. méd.* 23, 128 and 136), on the other hand, it is not a constant constituent. Herberger (*Jahrb. pr. Pharm.* 2, 178) found in most cases, but not always, both iodine and bromine (the quantity of which he determined), sometimes iodine without bromine, sometimes neither one nor the other. See also Brandes (*N. Br. Arch.* 13, 156), Wackenroder (*N. Br. Arch.* 24. 145),

Chevallier (*J. Chim. méd.* 22, 695), L. Gmelin (*Ann. Pharm.* 29, 218, and 31, 321), Girardin and Preisser (*Compt. rend.* 14, 618), also Marder (*N. Br. Arch.* 13, 153) and Kummell (*N. Br. Arch.* 32, 99), the last two of whom found no iodine in cod-liver oil.—Water, alcohol, and ether do not extract the iodine and bromine (Herberger), whereas iodide of potassium added to cod-liver oil is dissolved out by alcohol (Stein, *J. pr. Chem.* 24, 306) When cod-liver oil is carefully charred, the residue is found to contain bromine and iodine, but not the whole quantity present in the oil (Herberger). When the oil is saponified, the iodine passes into the under-lye (L. Gmelin); when the oil is saponified, the aqueous solution of the potash-salt precipitated by sulphate of magnesia, and the liquid filtered, the iodine passes into the filtrate, and cannot be detected by carbonising the magnesia-soap and exhausting the residue with nitric acid (Gräger, *N. Br. Arch.* 26, 60). The iodine neither passes into the under-lye, nor into the acid liquid obtained on decomposing the soap, but remains associated with the fatty acids (Stein). The only way of detecting it is to saponify the oil and carbonise the soap (De Jongh). Ludwig also (*Apoth. Ver. Zeit.* 1, 181) obtained, on the one hand, glycerin free from iodine, on the other soap containing iodine. *Winkler's* statement (*Jahrb. pr. Pharm.* 25, 110) that cod-liver oil, when saponified by potash or lead-oxide, does not yield glycerin, but instead of that substance, Winckler's propylic oxide or propylic acid, does not agree with the earlier experiments of De Jongh and Marder; neither is it confirmed by the observations of Ludwig.

When cod-liver oil which has been exhausted with water is saponified, the soda-soap decomposed by neutral acetate of lead, and the lead-salt exhausted with ether, margarate of lead remains undissolved, while the ether takes up De Jongh's *gaduin*, besides oleate of lead. The oleate of lead is reconverted into soda-salt, the latter dissolved in hot alcohol of $30°$ B, and the solution cooled to $0°$; the gaduin then remains dissolved, and may be separated from the solution by sulphuric acid. This gaduin is a dark-brown, friable, inodorous and tasteless acid, which is insoluble in water and in nitric acid, but dissolves with red colour in oil of vitriol, and may be reprecipitated by water or alkalis. It emits when burnt the odour of acetic acid and of cod-liver oil; contains 68·91 p. c. C., 7·51 H., and 23·58 O.; its lead-salt contains 51·73 C., 5·49 H., 27·31 PbO.; and its silver-salt 50·21 C., 5·37 H., 27·63 AgO. De Jongh gives the formulæ $C^{35}H^{23}O^9$ and $C^{35}H^{42}MO^9$.

The turbid residue of a light brown cod-liver oil, deposited at $5°$ after previous warming, large crystalline laminæ, which were collected on linen, pressed, saponified with potash, and purified by salting out the soap, decomposing the aqueous solution with basic acetate of lead, exhausting the lead-plaster with ether, and decomposing it with warm aqueous hydrochloric acid. These crystals consist of Luck's *Gadinic acid*, which, after decolorisation with animal charcoal, and recrystallisation from alcohol, forms thin shining laminæ, melting at $63°$ or $64°$, and solidifying in very long needles at $60°$. — The potash-salt forms large shining laminæ. The baryta-salt dried in vacuo, contains 57·22 p. c. C., 9·58 H., 7·75 O., and 25·45 BaO.; the silver salt, 50·85 p. c. C., 8·34 H., 6·86 O., and 33·95 AgO., agreeing nearly with Luck's formula of the acid $C^{29}H^{29}O^4$. The acid dissolves sparingly in cold, easily in hot alcohol (Luck, *N. Jahrb. Pharm.* 6, 249; *Chem. Centr.* 1857, 191). These data do not accord either with any other of the individual known fatty acids, or with any mixture of them (Kr.).

Cod-liver oil kept in a closed vessel for 10 years, contained 77·44

p. c. C., 11·27 H., and 11·29 O.; the same after keeping for 10 years with access of air, contained 72·71 p. c. C., 10·14 H., and 17·15 O.; it had therefore taken up a quantity of oxygen, amounting to 5·52 p. c. of its weight, or 51·6 times its volume. At the same time it had become viscid and turbid (Attfield, *Chem. News*, 2, 99 ; *Rép. Chim. pure*, 2, 433 ; *Kopp's Jahresb.* 1860, 325). — *Oil of vitriol* colours cod-liver oil black (Girardin & Preisser). A mixture of 2 pts. oil of vitriol and 1 pt. cod-liver oil, becomes hot, blood-red, black and thick after several days, and smells of sulphurous acid (Marder). A few drops of oil of vitriol colour cod-liver oil violet, red-brown, and finally black ; seal and whale-oil treated in like manner immediately become brown and black (Kümmell, *N. Br. Arch.* 32, 99). — A well shaken mixture of 5 vol. cod-liver oil and 1 vol. sulphuric acid of sp. gr. 1·475 or 1·53 becomes purple after 15 minutes; a mixture of the oil with the same proportion of sulphuric acid of sp. gr. 1·035, dark-brown. Nitric acid of sp. gr. 1·22, used instead of sulphuric acid, does not colour the oil; but nitric acid of sp. gr. 1·33 reddens it; so likewise does syrupy phosphoric acid, whereas nitrosulphuric acid turns it brown (Calvert, *J. pr. Chem.* 61, 354).

When cod-liver oil is mixed with oil of vitriol, and the mixture is heated with excess of alkali, an odour of oil of rue is emitted ; the mixture, diluted with water and distilled, gives off a light yellow oil, having the smell of oil of rue, lighter than water, and boiling at about 300°. If the mixture of cod-liver oil and oil of vitriol is kept for some days and then distilled with lime and water, it yields a milky distillate, having the odour of peppermint (Wagner, *J. pr. Chem.* 46, 155; *comp.* xiv. 451). — When cod-liver oil is distilled with potash-ley, a watery distillate is obtained, having the odour of train-oil, and containing Winckler's propylic oxide (Wagner). Cod-liver oil heated with $\frac{1}{5}$ of its volume of soda-ley of sp. gr. 1·34, acquires a red colour (Calvert).

With alcoholic ammonia it forms a large quantity of amide, melting at 80° (Carlet). Rowney (*J. pr. Chem.* 67, 160) obtained a small quantity of amide, melting at 93°, becoming solid and transparent at 94°, containing on the average, 75·69 p. c. C., 12·99 H., and 4·35 N., and easily soluble in alcohol.

10. *Ray-liver oil.* — Obtained by boiling the livers of *Raya clavata* and *R. batis* with water. Pale yellow ; smells like fresh whale oil. Sp. gr. 0·928. Neutral. It deposits a white substance when exposed to the air, more quickly when chlorine is passed into it. With oil of vitriol it acquires a dark-red colour, changing after a quarter of an hour's standing and stirring to light violet ; 100 pts. alcohol of 89 p. c. dissolve 1·5 pts. of the oil at 10°, and 14·5 pts. at the boiling heat. 100 pts. boiling ether dissolve 88 pts., the greater portion of which is deposited on cooling. By saponification, oleic acid, margaric acid, glycerin, and delphinic acid having an offensive odour, are obtained. A litre of the oil contains 0·18 grm. iodide of potassium. (Girardin & Preisser, *N. J. Pharm.* 1, 503 ; *Compt. rend.* 14, 618; *J. pr. Chem.* 26, 399.) See also Gobley (*N. J. Pharm.* 5, 306), who found 0·21 grm. iodide of potassium in the litre. The oil contains phosphorus and sulphur (Gobley, *N. J. Pharm.* 6, 25 ; *J. pr. Chem.* 33, 374).

11. *Burbot-fat.* — From the liver of *Gadus Lota* or *Lota vulgaris.*

Pale yellow; has an odour fainter than that of train-oil. Contains neither iodine nor bromine (Herberger, *Jahrb. pr. Pharm.* 2, 178).

Oxygen-nucleus $C^{32}H^{26}O^4$.

Digitaliretin.

? $C^{32}H^{26}O^6 = C^{32}H^{26}O^4,O^2$.
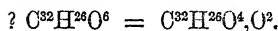
Walz. *N. Jahrb. Pharm.* 9, 304 ; further 10, 326.

See *Digitalin* (p. 331).

Formation. 1. Digitaletin is resolved, by boiling with dilute sulphuric acid, into digitaliretin and sugar, paradigitaletin being formed at the same time. — 2. When digitalin is boiled with dilute sulphuric acid, sugar and digitaletin are produced, the latter then decomposing further, as in 1.

Preparation. When 4 gr. digitaletin are boiled with 200 gr. water and 6 gr. oil of vitriol, for several days, or as long as the deposit still contains undecomposed digitaletin (sparingly soluble in cold alcohol), a yellow resin separates out, which, when washed with water, then dried, and treated with absolute ether, gives up to this solvent, digitaliretin, amounting to half the weight of the digitaletin used, while 0·52 gr. para-digitaletin remains behind in the form of a yellowish brown powder. By spontaneous evaporation of the ether, the digitaliretin is obtained as a loose powder.

When 304 pts. digitalin, dissolved in 20 pts. of water, are boiled with 500 pts. oil of vitriol till completely decomposed, the precipitate then washed to remove adhering acid, and treated in alcoholic solution with basic acetate of lead, a colourless solution is obtained which (after removal of the lead. Kr.) dries up to a cauliflower-like, indistinctly crystalline mass. This, when treated with absolute ether, gives up 130 pts. of digitaliretin, while 59 pts. paradigitaletin remain undissolved.

Yellowish-white powder, having a bitter, not sharp taste, and melting at 60° to a resin.

									Walz. mean.	
	Calculation according to Walz.								*a.*	*b.*
32 C	....	192	....	72·18	40 C	....	240	.... 71·42	72·1	72·10
26 H	....	26	....	9 77	32 H	....	32	.... 9·52	9·8	9·81
6 O	....	48	....	18·05	8 O	....	64	.... 19·06	18·1	18·09

$C^{32}H^{26}O^6$ .... 266 .... 100·00 $\qquad$ $C^{40}H^{32}O^8$ .... 336 .... 100 00 .... 100·0 .... 100·00

a. from digitatelin ; *b.* from digitalin.

Walz is undecided between the two formulæ just given. If the first be adopted, the decomposition of digitalin may be explained by supposing that sugar and digitaletin are first formed :

$$C^{56}H^{48}O^{28} = C^{12}H^{10}O^{10} + C^{44}H^{38}O^{18},$$
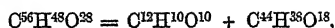
the latter being further resolved, either into digitaliretin and sugar :

$$C^{44}H^{38}O^{18} = C^{32}H^{26}O^6 + C^{12}H^{12}O^{12},$$

or into paradigitaletin and water,

$$C^{44}H^{38}O^{18} = C^{44}H^{34}O^{14} + 4HO.$$
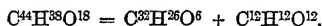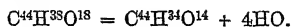
Assuming these formulæ, the composition of the acrid principles A and B (xiv, 532) may be represented by the formulæ $C^{32}H^{26}O^6,2HO$, and $C^{32}H^{26}O^6,3HO$, whereas, if the second formula of digitaliretin ($C^{40}H^{32}O^8$) be adopted, the formulæ $C^{40}H^{32}O^8 + 2HO$ and $+ 3HO$ are obtained.

Digitaliretin is quickly dissolved by strong *nitric acid*, forming a dark yellow solution, which, when evaporated, leaves a golden-yellow nitro-compound.

Insoluble in *water;* dissolves with reddish-yellow colour in *oil of vitriol*, and is precipitated therefrom by water; insoluble in *hydro-chloric acid, ammonia,* and *potash-ley.*

Dissolves in *alcohol* and in *ether.*

Glucosides of Digitaliretin.

1. Digitaletin.

$$? C^{44}H^{38}O^{18} = C^{32}H^{26}O^6,C^{12}H^{12}O^{12}.$$
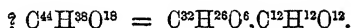
WALZ. *Jahrb. pr. Pharm.* 21, 33. — *N. Jahrb. Pharm.* 8, 322; further, 9, 307; further, 10, 319.
DELFFS. *N. Jahrb. Pharm.* 9, 26.

Formerly called *Digitalin* by Walz, and spoken of for the most part by that name in the memoirs above cited. (See *Digitalin.*)

Occurrence. — In purple and yellow fox-glove (*Digitalis purpurea* and *D. lutea.*

Preparation. — A. *From Fox-glove leaves.* When the dried and pulverised leaves are freed from chlorophyll by complete exhaustion with ether, and the undissolved residue is further exhausted with alcohol, the alcoholic tincture yields, with alcoholic sugar-of-lead, a copious yellow-green precipitate; and the filtrate, freed from excess of lead by hydrosulphuric acid and decolorised by animal charcoal, yields, when left to evaporate over oil of vitriol, crystals and nodules of digitaletin, amounting to 0·43 p. c. of the weight of leaves used (Walz). The mother-liquor retains digitalin in solution, which may be obtained by precipitating with tannic acid, dissolving the precipitate in alcohol, digesting the alcoholic solution with hydrated oxide of lead till the whole of the tannic acid is precipitated, and evaporating the filtrate. From the digitalin thus obtained, ether extracts only traces of acrid principle and fat (Walz).

B. *From crude Digitalin* (p 331). 1. The substance is freed by absolute ether from the body designated by Walz as digitalicrin (xiv. 530); the digitalin is then dissolved out by cold water; and the remaining digitaletin, after being washed with cold water, is purified by re-crystallisation from boiling alcohol of sp. gr. 0·83 (Walz).

2. Crude digitalin is triturated to a pulp with cold alcohol of 70 p. c.;

the pulp is left to drain upon a filter; and the residue is washed on the filter with small quantities of alcohol, as long as the alcohol which runs off appears coloured when viewed in rather thick layers. When the residue is dissolved in boiling alcohol of 80 to 85 p. c., the solution filtered as hot as possible, deposits on cooling, dazzling white flakes of digitaletin, only a small quantity of which remains dissolved in the mother-liquor (Delffs).

Properties. White, crystalline nodules (Walz). Microscopic roundish grains, having the diameter of the corpuscles of human blood (Delffs). Its solution in cold water has a strong, bitter taste (Walz). According to a later statement of Walz, water heated with digitaletin is tasteless. If dried at 45° and then further heated, it gives off 2 p. c. water at 100°, melts at 175°, and begins to decompose, with evolution of acid vapours, at 206°.

| | | | Walz (mean). | | | Delffs. |
			earlier.	later,		mean.
44 C	264	59·19	59·40	59·1		59·08
38 H	38	8·52	9·14	8·8		8·69
18 O	144	32·29	31·46	32·1		32·23
$C^{44}H^{38}O^{18}$	446	100·00	100·00	100·0		100·00

Walz original gave the formula $C^{10}H^9O^4$.

Decompositions. 1. Digitaletin *heated* on platinum-foil, melts, puffs up, and gives off white fumes, which burn with a slight deposit of soot (Walz). — 2. By boiling with dilute *sulphuric acid*, it is resolved into sugar and digitaliretin, a certain quantity of paradigitalin being formed at the same time:

$$C^{44}H^{38}O^{18} = C^{12}H^{12}O^{12} + C^{32}H^{26}O^6 \text{ (Walz)}.$$
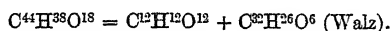
The formation of sugar by boiling digitaletin with dilute sulphuric acid, had previously been observed by Delffs. — 3. Digitaletin immersed in *oil of vitriol*, assumes a dark-red colour, and then dissolves completely. Water renders the solution turbid, then colours it olive-green, and dissolves the whole. — 4. Digitaletin dissolves in fuming *nitric acid*, with yellow colour, and without perceptible decomposition; and water subsequently added, separates a jelly and then white flocks.

Combinations. Digitaletin dissolves at mean temperature in 848 pts., at 45° in 500 pts., and at the boiling heat in 222 pts. *water,* and separates from the last solution in nodules on cooling. — It dissolves in cold *hydrochloric acid* of sp. gr. 1·21, and is precipitated by water. — It dissolves without coloration in aqueous *ammonia,* and is separated again by evaporation, or by addition of water.

It dissolves in 3½ pts. *alcohol* of sp. gr. 0·85 at mean temperature, in 2⅓ to 2½ pts. at the boiling heat, in 3⅓ pts. absolute alcohol at 15°, and in 2 pts. at the boiling heat. — It dissolves in 1960 pts. *ether* at 15°, and in 1470 pts. boiling ether.

Tannate of Digitaletin. — Obtained by precipitating aqueous digitaletin with tannic acid. After drying it is yellowish-brown, and when rubbed to powder forms a mass resembling tannic acid; it is insoluble in water, but soluble in alcohol (Walz).

2. Paradigitaletin.

$$? \ C^{44}H^{34}O^{14} = C^{32}H^{24}O^4,C^{12}H^{10}O^{10}.$$
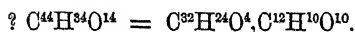
WALZ. *N. Jahrb. Pharm.* 9, 305.

Obtained, together with sugar and digitaliretin, by the decomposition of digitaletin and digitalin by dilute sulphuric acid (p. 328), and purified by recrystallisation from alcohol.

Shining, yellowish, tasteless mass, not decomposed at 100°.

					Walz. mean.		
						a.	b.
44 C	264		64·39		64·5		64·54
34 H	34		8·39		8·3		8·30
14 O	112		27·22		27·2		27·16
$C^{44}H^{34}O^{14}$	410		100·00		100·0		100·00

a. obtained from digitaletin, *b* from digitalin. — Differs from digitaletin by containing 4 at. less water.

Paradigitaletin melts and *burns* at high temperatures, leaving charcoal. — *Oil of vitriol* dissolves it, first with brownish, then with fine red colour; and water added to the solution throws down greenish flakes. — Fuming *nitric acid* dissolves it quickly, and, with evolution of gas, forming a solution which becomes cloudy on addition of water.

Paradigitaletin is insoluble in *water*. — It dissolves in warm *hydrochloric acid* of sp. gr. 1·16, and remains in its original state when the solution is evaporated. It dissolves slowly in cold, rapidly in warm *potash-ley*, and is precipitated by acids. It does not dissolve in aqueous ammonia, and is not altered by evaporation therewith.

Soluble in *alcohol*, insoluble in *ether*.

3. Digitalin.

$$? \ C^{56}H^{48}O^{28} = C^{32}H^{26}O^6,C^{24}H^{22}O^{22}.$$
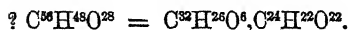
HOMOLLE (1845). *N. J. Pharm.* 7, 57; abstr. *Berzel. Jahresber.* 26, 720.

O. HENRY. *N. J. Pharm.* 7, 460; abstr. *Berzel. Jahresber.* 26, 723.

NATIVELLE. *J. Chim. méd.* 21, 61; abstr. *Berzel. Jahresber.* 26, 724.

KUSMANN. *J. Chim. méd.* 22, 377.

L. A. BUCHNER. *Repert.* 88, 173.

LEBOURDAIS. *N. Ann. Chim. Phys.* 24, 58; *Ann. Pharm.* 67, 251; *J. pr. Chem.* 45, 363.

HOMOLLE & QUEVENNE. *Mémoires sur la Digitaline;* abstr. *N. Repert.* 9, 1.

A. BUCHNER, SEN. *N. Repert.* 9, 38.

G. F. WALZ. *Jahrb. pr. Pharm.* 12, 83; further, 14, 20; further, 21, 29; further, 24, 86. — *N. Jahrb. Pharm.* 8, 322; further, 9, 302; further, 10, 319.

DELFFS. *N. Jahrb. Pharm.* 9, 25.

Attempts to isolate the bitter principle of the purple fox-glove (*Digitalis purpurea*) were made many years ago by Leroyer (*Bibl. univ.* 26, 103; *Schw.* 42, 110), Dulong d'Astafort (*J. Pharm.* 13, 379; *N. Tr.* 16, 2, 209; *Berz. Jahresber.* 8, 278), Meylink (*Repert.* 28, 237), Planiowa (*Zeitschr. Math. Phys.* 4, 450), Watson J. Welding (*J. of Philad. Coll. of Pharm.* 1833; abstr. *J. Pharm.* 20, 98; *Ann. Pharm.* 13, 212), Radig (*Ehrmann, das Neueste &c. der Pharm. Wien.* 1834, 2, 142), Lancelot (*Ann. Pharm.* 12, 251), Brault & Poggiale (*J. Pharm.* 21, 130), B. Trommsdorff (*N. Br. Arch.* 10, 113), A. Henry (*J. Scienc. Phys.* 4, 74) and Bonjean (*N. J. Pharm.* 4, 25); but all these authors describe as Digitalin chiefly the ethereal or alcoholic extract, or the substances precipitated by acids from infusions of digitalis. Homolle first obtained a purer product, and must therefore be regarded as the discoverer of digitalin. Walz, following chiefly, but not wholly, the directions given by Homolle, obtained his crude digitalin, which he afterwards (*see below*) resolved into digitalin, digitaletin, digitaliretin, and other substances, some of which appear to be identical with those subsequently obtained by Homolle & Quevenne from Homolle's digitalin. Other chemists, adopting other modes of preparation, obtained substances of different properties — which they nevertheless describe as digitalin. These relations are still more confused by the circumstance that the French make a distinction between *digitaline* and *digitalin;* that Kossmann's *digitaline* again does not agree with that of Homolle & Quevenne; and that Walz at first designated his digitaletin as digitalin, regarding it as identical with Homolle's digitalin, whereas he now gives the name digitalin to the bitter substance, $C^{56}H^{45}O^{28}$, formerly called *digitasolin*. For these reasons, the products obtained by different chemists from digitalis, will here be described separately (Kr.).

On a liquid volatile alkaloïd from digitalis, obtained in the same manner as conine from hemlock, and regarded by W. Engelhardt (*Zeitschr. Chem. Pharm.* 5, 722) as the active principle of the plant, further communications may be expected.

Occurrence. In the leaves of *Digitalis purpurea.* — The seed and capsules likewise contain digitalin (A. Buchner, sen.) Also in *Digitalis lutea*, at and after flowering time.

A. Walz's *Digitalin.* Formerly known as digitasolin, and designated as such in the memoirs above cited.

Preparation. The green parts of the fox-glove plant coarsely pulverised are exhausted in a Real's press with 8 pts. alcohol of sp. gr. 0·852; the alcohol is distilled from the clear tincture in the water-bath; the residue is treated with water so long as it imparts a bitter taste to that liquid; and the united extracts are digested with levigated oxide of lead and a small quantity of basic acetate, till a filtered sample is no longer clouded by the basic acetate. The liquid is then filtered; the greater part of the dissolved lead is removed by dilute sulphuric acid, the rest by sulphate of ammonia; the solution is neutralised with aqueous ammonia and filtered; the precipitate well washed; and the solution precipitated with aqueous tannic acid (less advantageously with infusion of gall-nuts or oak-bark). The precipitate, well washed and pressed, is triturated with recently precipitated hydrate of lead, and exhausted with alcohol; the alcoholic extracts are freed from a small quantity of dissolved lead by hydrosulphuric acid, and from the greater part of the alcohol by distillation; and the residue is left to evaporate slowly.

The aqueous decoction of the plant may also be treated, as above described, instead of the alcoholic extract; but the digitalin thus obtained is more coloured, and requires to be purified by treating its alcoholic solution with a small quantity of blood-charcoal (Walz).

2. The alcoholic extract of the comminuted leaves is agitated with basic acetate of lead, and the yellowish green filtrate is precipitated

with hydrosulphuric acid. After separating the sulphide of lead, the alcohol is distilled off; the residue is exhausted with ether; the portion insoluble in ether is taken up by water, and this solution is precipitated with tannic acid. The washed precipitate dissolved in alcohol and decomposed by basic acetate of lead, leaves nearly white digitalin as residue (by what treatment? Kr.) (Walz).

3. The recently dried, coarsely bruised leaves are completely exhausted with alcohol; the resulting tinctures are freed from alcohol by distillation; and the residue, after being evaporated to the thickness of an extract, is exhausted with water containing $\frac{1}{30}$ of acetic acid. The acetic solution is shaken up with purified animal charcoal, filtered, neutralised with ammonia, and precipitated by tannic acid. The dried precipitate is exhausted with alcohol of 90 p. c.; the extracts are again decolorised and freed from alcohol by distillation; and the dry residue is twice washed with water. The undissolved portion is dried, washed by agitation with ether, dissolved in warm alcohol of 90 p. c., and the solution is left to evaporate (Wittstein). This process yields from 1·25 to 1·43 p. c. digitalin (Wittstein), 0·7 to 0·8 p. c. (Walz).

According to Walz, the same product is likewise obtained by the following process. The aqueous extract of digitalis is exhausted with alcohol, filtered, mixed with tartaric acid to separate a small quantity of potash, decanted, and precipitated with neutral acetate of lead, and the excess of lead is removed from the filtrate by hydrosulphuric acid. The greater part of the alcohol is distilled off, and the residue is evaporated to dryness and treated with acetic acid, which dissolves the bitter principle, and leaves it, on evaporation, as a reddish-yellow bitter mass, ropy when warm, hard and brittle when cold, easily soluble in water and alcohol, insoluble in ether, precipitable by basic acetate of lead and by tannic acid (Dulong d'Astafort). The bitter substance obtained by Dulong differs but little from digitalin, but is contaminated with alkalis (Walz).

Crude digitalin prepared by either of these processes still contains: 1. Certain substances which may be extracted by ether (xiv, 530—532), viz., digitaloïc acid, the acrid principles of digitalis, A and B, and digitalis-fat (all included by Walz under the term digitalicrin or digitalacrin). 2. A substance insoluble in cold water, viz., digitaletin. — To separate these substances and prepare pure digitalin, the following process is adopted:—

Crude digitalin is exhausted with absolute ether; the residue is covered with 8 pts. of water, which dissolves the digitalin, leaving the digitaletin at the bottom in the form of a white powder; and the undissolved portion is collected and thoroughly washed with cold water. The solution is either (a) decolorised with animal charcoal, filtered, and evaporated to dryness;—or better (b), precipitated by tannic acid; the precipitate washed, dried at a gentle heat, and triturated with an equal quantity of hydrated oxide of lead, and with water; the solution, after standing for some time, filtered from the undissolved portion; and the latter thoroughly washed. The solution, when carefully evaporated, leaves a nearly colourless jelly, which, when perfectly dry, may be triturated to a yellowish powder.

Walz afterwards suspected that digitalin thus prepared might still retain digitaletin: he therefore now dissolves the precipitate produced by tannic acid (as in b) in warm alcohol; agitates the solution with basic acetate of lead till all the tannin is removed; precipitates the excess of lead by hydrosulphuric acid; and leaves the filtrate to evaporate.

Properties. Yellowish amorphous mass which cannot be obtained white, even after repeated solution in water, precipitation with tannic acid, and decomposition of the precipitate with basic acetate of lead (Walz). Remains unaltered at 100°, melts at 137·5°, and decomposes at 300°. Tastes strongly bitter (Walz). For its physiological properties, see below. Molecular rotation, left, $[\alpha]r = 30$ (Buignet, *N. J. Pharm.* 40, 252).

| | Dried. | | | Walz (mean). | |
				earlier.	later.
56 C	336	55·26		55 95	55·2
48 H	48	7·90		8·12	7·9
28 O	224	36·84		35·93	36·9
$C^{56}H^{48}O^{28}$	608	100 00		100·00	100 0

Walz formerly assigned to it the formula $C^{19}H^{16}O^9$.

Decompositions 1. Digitalin heated on platinum-foil, *burns* without residue.—2. With cold *oil of vitriol,* it becomes red-brown, then on dilution with water, dirty greenish brown, without precipitation of much of the dissolved matter. — By boiling with *dilute sulphuric acid,* it is resolved into sugar, digitaliretin and paradigitaletin. 100 pts. digitalin yielded 42·8 p. c. sugar, 39·5 p. c. digitaliretin, and 19·3 p. c. paradigitaletin. Hence Walz supposes that the digitalin is first resolved into sugar and digitaletin ($C^{56}H^{48}O^{28} = C^{12}H^{10}O^{10} + C^{44}H^{38}O^{18}$); and that the latter is partly converted, by abstraction of 4 at. water, into paradigitaletin, partly resolved into digitaliretin and sugar ($C^{44}H^{38}O^{18} = C^{12}H^{12}O^{12} + C^{32}H^{26}O^6$). — 3. Digitalin is dissolved by *hydrochloric acid* of sp. gr. 1·2, and is partly precipitated on diluting the solution with water (Walz). By boiling with dilute hydrochloric acid, it yields sugar (Ludwig) (*N. Br. Arch.* 82, 138). — 4. It dissolves in fuming *nitric acid* with reddish yellow colour, and slight evolution of red vapours; and water added to the solution, first forms a jelly, afterwards separates a yellow deposit (Walz).

Combinations. Digitalin dissolves in 125 pts. cold and 42 pts. boiling water. — The statement of Abl (*Oesterr. Pharm. Zeitschr.* 8, 201) that digitalin dissolves in 1,290 pts. water at 19° appears to relate to digitaletin. Digitalin dissolves in aqueous *ammonia* with rose-red colour, changing to brownish, is precipitated by water, and remains apparently unaltered when the ammonia evaporates. It dissolves at mean temperature in $2\frac{1}{2}$ pts. absolute *alcohol,* or spirit of sp. gr. 0·85, at the boiling heat in $1\frac{2}{3}$ to 2 pts. — It dissolves in 20,000 pts. of *ether* at 15°, and in 10,000 pts. boiling ether (Walz). — In 80 pts. *chloroform* at $17\frac{1}{3}$° (Schlimpert, *N. Br. Arch.* 100, 152).

Tannate of Digitalin. From an aqueous solution of digitalin tannic acid throws down a flocculent precipitate, which soon adheres together into a resinous transparent mass; this, when dry, becomes of a brownish-yellow colour, and can be rubbed down to a light grey powder; it is soluble in 500 parts of cold, or 300 parts of boiling water; in the latter it melts to a soft resin containing 45 per cent. of digitalin (Walz).

B. Homolle's *Digitalin.* This substance was subsequently designated

by Homolle & Quevenne as *la Digitaline*, and shown to be a mixture. According to Walz, it is identical with digitaletin (p. 328).

Two pounds of roughly-powdered fox-glove leaves are moistened with water, and exhausted in a percolator; the aqueous extract is precipitated by basic acetate of lead; carbonate of soda is added to the filtrate as long as it forms a precipitate; the lime is thrown down by oxalate of ammonia; and the magnesia by phosphate of soda and ammonia. The solution is filtered off, and precipitated with excess of tannic acid; the precipitate is collected, washed with a little cold water, and while still moist, mixed with half its weight of washed litharge; and the soft mass is drained on blotting-paper, dried at a gentle heat, pounded, and digested in boiling alcohol. The alcoholic solution, evaporated at a gentle heat, leaves digitalin, which may be freed from deliquescent salts by washing with water, dissolved in boiling absolute alcohol, treated with animal charcoal, and obtained as a yellow granular mass, by spontaneous evaporation of the filtrate. This is pounded, drenched with ether for 24 hours, and afterwards boiled in it. The undissolved portion is Homolle's digitalin, a small quantity of which is likewise deposited from the ethereal solution by spontaneous evaporation, in white crusts, but mixed with a greenish oil and slender needles of another substance (Homolle).

Properties. White warty masses or fine scales, inodorous, but having a very bitter taste. The dust causes sneezing. Neutral. A dose of 0·01 gramme taken internally considerably depresses the pulse, and causes headache, confused vision, and debility. — It prevents fermentation in a solution of sugar to which yeast has been added (A. Buchner, sen.).

Decompositions. 1. On being heated to 180°, it becomes yellow; at 200° it turns brown, softens, and swells up; then at 200° [?] sinks down again, and now tastes less bitter, but sharper and astringent. — 2. Digitalin is inflammable, and burns with a sooty flame.—3. With *oil of vitriol*, it forms at once a dark solution, exhibiting after a few days, a crimson colour when viewed in thin layers, and becomes green on addition of a little water. — 4. *Phosphoric acid* turns it green, but does not dissolve it. — 5. It is immediately dissolved by strong *hydrochloric acid*; the solution in a few moments assumes an emerald green colour, and after standing for an hour, deposits a green powder, which becomes dark green in a few days. — 6. Treated with *nitric acid*, it gives off nitrous fumes, and forms a yellow solution, which afterwards assumes a golden colour. — 7. When boiled down with *solution of potash*, it loses its bitter taste, and then tastes astringent (Homolle).

Combinations. Digitalin is soluble in about 2,000 parts of cold and 1,000 parts of boiling *water* :—It dissolves unchanged in concentrated acetic acid; in dilute *acids* not more plentifully than in water, and does not form salts with them. The aqueous solution does not give precipitates with solutions of metallic salts (Homolle). It is easily soluble in *alcohol* and in mixtures of alcohol and water.—It dissolves in 1,250 parts of cold anhydrous *ether* of sp. gr. 0·726.—The alcoholic solution of digitalin is precipitated by tannic acid (Homolle).

O. Henry treats the alcoholic extract of digitalin with a mixture

of 1 part acetic acid and 32 parts water at 40° to 50°, decolorises the solution with animal charcoal, filters, neutralises with ammonia, and precipitates with decoction of nutgalls. The precipitate is mixed with a third of its weight of litharge and digested in 2 measures of alcohol of sp. gr. 0·83 ; and the liquor, separated by filtration and pressing the residue, is treated with animal charcoal and evaporated to dryness after filtration. The residue is now washed two or three times with ether, the digitalin then remaining. 1 kilogramme of the dry leaves yields from 9 to 10 grammes of digitalin, exhibiting the properties described by Homolle (O. Henry).

The following description by Kosmann (*N. J. Pharm.* 38, 1), appears to refer to Homolle's digitalin, B.

Properties. Hydrate of digitalin (? Kr.) loses 10·07 per cent. of water at 100° without further change and is then highly hygroscopic. It is free from nitrogen.

			Calculation according to Kosmann.		Kosmann. *mean, at* 100°.
54	C	....	324	.... 53·20	.... 52·70
45	H	....	45	... . 7 39	.... 7·52
30	O	....	240	...... 39·41	... . 39·78
	$C^{54}H^{45}O^{30}$	....	609	.... 100 00	.... 100·00

So according to Kosmann.

Decompositions. Digitalin boiled with dilute sulphuric acid is resolved into Kosmann's digitaliretin and fermentable sugar :

$$C^{54}H^{45}O^{30} + 4HO = C^{30}H^{25}O^{10} + 2C^{12}H^{12}O^{12}.$$
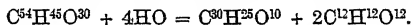
100 parts digitalin gave as an average 57·41 pts. sugar and 46·67 pts. digitaliretin. During the ebullition, the smell of digitalin is perceptible.—2. It dissolves slowly when boiled in *soda-ley* and is converted into digitalic acid without formation of sugar. 100 pts. digitalin yield 116·3 digitalate of soda.

C. Homolle and Quevenne's *Digitaline.*—The digitalin prepared by Homolle is decomposible into digitalin, digitaline, and digitalose. When Homolle's digitalin is treated with alcoholic ether of 0·78 sp. gr. the digitaline and digitalose are dissolved and the digitalin is left behind; and if the filtrate be then evaporated to dryness, and the residue treated with alcohol of 60°, the digitaline dissolves, leaving the digitalose. The digitaline may be recovered by evaporating the solution.

Properties. Non-crystalline scales, or pale-yellow, transparent, friable resin. It withstands the action of the air, has a peculiar faint odour and very bitter taste. Neutral. For its physiological action see *N. Repert.* 9, 20.

It behaves with hydrochloric like Homolle's digitalin.—Dissolves very sparingly in *water*, in all proportions in *alcohol*, in 100 parts *ether* of sp. gr. 0·727 at 9° at. (Homolle & Quevenne).

D. *Digitalin of Lebourdais.* — The aqueous solution of the extract of digitalis prepared with dilute alcohol, is precipitated with neutral acetate of lead, filtered, and shaken up with bone-black previously washed in acid, whereby the liquor loses its colour and bitter taste. On decanting

the liquor, washing the charcoal with water, exhausting it by boiling in alcohol, evaporating the weakly-coloured alcoholic solution over a water-bath, and leaving it to cool, a powder is deposited which is to be washed and dissolved in alcohol: the solution thus obtained yields crystals of digitalin by spontaneous evaporation. These are very bitter, neutral, and free from nitrogen. They dissolve in *oil of vitriol*, forming a beautiful purple solution, which, after some time, becomes brown and deposits a black substance. The purple solution becomes green on addition of water. The crystals are but sparingly soluble in *water*; they dissolve without colour in *hydrochloric* and in *nitric acid* or *alcohol*, with greater facility in proportion as it is more free from water, and but slightly in *ether* (Lebourdais).

E. *Digitalin of* Nativelle. — 500 gr. coarsely-powdered fox-glove leaves are exhausted in a percolator with alcohol of 50 p. c.; the dark-red tincture is evaporated on flat dishes in a current of air; and the residue is dissolved in a litre of warm water: tannate of digitalin then remains behind as a sticky mass, which is washed with a little water and removed. (This, when subjected to the following treatment, yields modified digitalin.) The solution is evaporated down to 4 litres; 1,000 grs. of basic acetate of lead is stirred well into it; the precipitate is separated by filtration; the greater part of the lead removed from the filtrate by animal charcoal, the remainder by sulphate of ammonia; and as much sulphate of ammonia is dissolved in the clear filtrate as it is able to take up. From this, after some time, the digitalin separates in white flakes, which, after 24 hours, are collected, washed with a satu-rated solution of sulphate of ammonia, and, after drying, dissolved in 8 parts of water, sulphate of lead then remaining undissolved. The solution is again precipitated by saturation with sulphate of ammonia, and the precipitate of digitalin is collected, dried, and drenched with alcohol of 95 p. c. The filtered solution, evaporated at a gentle heat, deposits the digitalin (Nativelle, *J. Chim. méd.* 21, 61; abstr. *Berz. Jahresb.* 26, 724.

The solution of the alcoholic extract, prepared according to 1, is precipitated with tannic acid, and hot water is poured upon the pre-cipitate till it melts, after which it is kneaded in warm water; 20 grs. of the still moist precipitate is then dissolved in 1 litre of warm water with the aid of 10 drops of solution of ammonia; the solution is pre-cipitated with neutral acetate of lead at 20° and filtered; and in case the filtrate is still coloured, basic acetate of lead is added to it. The lead is again removed by carbonic acid and sulphate of ammonia, and the digitalin is precipitated from the filtrate by saturation with sulphate of ammonia; it may then be purified like that obtained by method 1. (Nativelle).

Properties. Amorphous, translucent, friable resin, having a per-sistent, bitter, and pungent taste. The dust irritates the eyes, and causes sneezing. 0·1 gr. is poisonous to animals if it cannot be voided by vomiting. Neutral. Permanent in the air. Contains nitrogen.

Decompositions. 1. Heated on platinum-foil it melts, becomes coloured, and gives off aromatic vapours, which are inflammable, and burn with a sooty deposit. — 2. The diluted watery solution, after standing several days in a covered glass vessel, acquires the smell of

cumarin, then of bitter almonds, deposits white flocks, and becomes acid, but still tastes bitter and sharp. — 3. It is precipitated from its aqueous solution as modified digitalin (see below) by weak *acids*, slowly at mean temperatures, very quickly at the boiling heat. — 4. It dissolves in *nitric acid* and in *oil of vitriol* with dark-red colour. — 5. By contact with alkaline solutions, it loses its bitter taste, which is restored only in modified form by neutralisation with acids.

Combinations. Soluble in all proportions in cold *water*. — From a solution not too dilute, it is precipitated by *basic acetate of lead*, but not by the neutral acetate. — It is easily soluble in weak spirit, sparingly in absolute *alcohol*, insoluble in *ether*. It is precipitated from its aqueous solution by tannic acid in white flocks, which unite into a soft, translucent mass (Nativelle).

Nativelle describes a *modified digitalin* (perhaps identical with Walz's digitaliretin: Kr.). which he obtains by the following method: The extract obtained from 500 grs. fox-glove leaves is dissolved in 2 litres of water; the solution is precipitated by neutral acetate of lead; the dissolved lead is removed from the filtrate by hydrosulphuric acid; and the solution is again filtered and evaporated to three-fourths of its bulk. On addition of a little acetic acid, this liquor, after long standing, or immediately on being warmed, deposits the modified digitalin in translucent oily drops. — This modified digitalin likewise separates out when the tannate of digitalin, obtained as in E, is dissolved in weak alcohol, and precipitated by basic acetate of lead; and the filtrate, after being freed from lead by hydrosulphuric acid, is left to itself. — Or sufficient acetic acid is added to the solution of extract of digitalis in a small quantity of water, and the tannate of digitalin, which separates after some time, is treated as above described. This digitalin likewise tastes extremely bitter, but dissolves with difficulty in *water*, easily in *alcohol*, from which it separates in confused crystals by slow evaporation (Nativelle).

F. *Digitalin* (not *Digitaline*) of Kosmann (*J. Chim. méd.* 22, 377). Kosmann's digitaline is identical with Homolle's digitalin. — It occurs in small quantity in the common fox-glove (*Digitalis purpurea*). When dry fox-glove leaves are boiled in a small quantity of water, shining crystals of this digitalin may be seen on agitating the cooled decoction in sunshine. — Dry fox-glove leaves are exhausted with cold water, the solution is precipitated with terbasic acetate of lead, and the filtrate is treated for digitalin according to p. 34, B. The precipitate is washed, boiled for a quarter of an hour with solution of soda, and the brown filtrate is supersaturated with dilute sulphuric acid; it then deposits a flocculent precipitate, which is collected, washed, dried, and boiled with alcohol of 85 p. c. The alcoholic extract is evaporated; and the solid crystalline residue is treated six times with ether, which dissolves Kosmann's fatty acid of digitalis; it is then boiled with water, which removes the extractive matter and leaves a white flocculent substance undissolved. This substance collected, washed, and dissolved in boiling alcohol, separates partly on cooling, partly after further evaporation, in crystalline scales consisting of Kosmann's digitalin. — Scales, exhibiting under the microscope a pearly lustre, like that of boracic acid. Neutral. Free from nitrogen. Has a sharp taste.

On being heated it *burns* without residue, giving off white fumes

and condensing in yellow drops, which afterwards solidify in the crystalline form. It dissolves sparingly in *water*, and, when boiled in that liquid, imparts to it a pearly lustre ; the solution deposits white flocks on addition of dilute sulphuric acid. It dissolves in aqueous carbonate of soda, and is thrown down by acids. The aqueous solution gives a white precipitate with *neutral* and *basic acetate of lead*, not with *sesquichloride of iron* or *nitrate of silver*.

Dissolves freely in warm *alcohol*, not in *ether* (Kosmann).

G. *Digitalin* of Lancelot, L. A. Buchner and others.—Lancelot repeatedly exhausts the aqueous extract of digitalis at 40° with alcohol of 36°; evaporates to an extract; redissolves this extract; and adds to the solution 8 times its weight of dilute hydrochloric acid. By this means a yellow flocculent precipitate of digitalin is formed, which is increased by addition of water. The digitalin still remaining in solution may be precipitated from the filtrate by potash. The precipitates, washed and dissolved in alcohol, are treated several times with animal charcoal, whereby a nearly colourless solution is obtained which deposits yellow crystalline grains on evaporation.—This digitalin is sharp, permanent in the air, and has an alkaline reaction (probably on account of the alkali contained in it. *Walz*). *Oil of vitriol* turns it rose-red, then olive-green. It is soluble in *acids*, and is precipitated therefrom by water (Lancelot)—The digitalin thus obtained is, according to L. A. Buchner, a weak resin-acid. It is soluble in alkaline liquids and is precipitated by acids, even by acetic acid, but is re-dissolved by an excess of acetic acid. The alkaline solution loses its bitterness on standing, more quickly when warmed. It dissolves with difficulty in *water*, easily in *alcohol*, but is nearly insoluble in *ether* (Buchner). Buchner's description does not therefore agree with that of Lancelot.—Riegel (*N. Br. Arch.* 58, 290) purified the digitalin which he obtained by Lancelot's process with animal charcoal, according to the method given by Lebourdais (p. 336), and found it then to agree with that of Lebourdais.

Appendix to Digitaliretin and Digitalin.

1. Kosmann's *Digitaliretin* is formed by boiling digitalin (Homolle's?) or digitalic acid with acids (see page 336).

Perhaps the same as Walz's digitaletin (Kr.).

Digitalin is boiled with dilute sulphuric acid for many hours or until it is completely decomposed; the digitaliretin which separates is collected, washed and dried, then dissolved in boiling alcohol; and the filtrate is left to evaporate slowly, whereupon it solidifies in a granular mass, which may be purified by recrystallisation.

Properties. Shining plates, which at 169° begin to melt without further change. It reddens litmus slightly. Tastes bitter.

	Calculation according to Kosmann.			Kosmann. *mean.*
30 C	180	63·15		63 23
25 H	25	8 77		8·41
10 O	80	28 08		28·36
$C^{30}H^{25}O^{10}$	285	100 00		100 00

Kosmann erroneously calculates the composition of digitaliretin at 63·5 p. c. (Kr.)

It scarcely dissolves in water, but renders the liquid bitter. — It does not dissolve, either in aqueous *ammonia* or in *potash-ley*. The alcoholic solution produces scarcely any precipitate in an alcoholic solution of neutral acetate of lead, but yields with it, on evaporation, a granular precipitate, while ammonia added to the supernatant acid liquid throws down white flocks, which disappear on being heated, and re-appear on cooling. With *basic acetate of lead* it forms a crystalline, and with *ferrous sulphate* a pale yellow precipitate. — With *sulphate of copper*, digitaliretin forms a sky-blue precipitate, which, when dried at 100°, contains 42·27 p. c. digitaliretin, 5·9 p. c. oxide of copper, and 51·8 p. c. of terbasic sulphate of copper, and from which alcohol extracts the whole of the digitaliretin. — The solution of digitaliretin slowly produces turbidity in a solution of *nitrate of silver* to which alcohol has been added, and precipitates shining scales which soon turn brown.

Digitaliretin dissolves sparingly in cold, easily in boiling *alcohol* of 90 p. c., and sparingly in *ether* (Kosmann, *N. J. Pharm.* 38, 1).

2. Digitalinic Acid.

KOSMANN. *N. J. Pharm.* 38, 14.

Formation. By boiling digitalin B with soda-ley.

Preparation. Digitalin is boiled for 1¼ hours with a solution of soda of 36° (Baumé), the water which evaporates being replaced; the liquid is nearly neutralized with dilute sulphuric acid, and evaporated to dryness; the residue is exhausted with boiling alcohol; and the filtrate is evaporated. It then deposits digitalinate of soda, which is decomposed by a slight excess of dilute sulphuric acid, and the flocculent precipitate which separates is collected and crystallised from boiling alcohol. When an alkaline solution of digitalin, after boiling and cooling, is at once precipitated with excess of dilute sulphuric acid, the greater part of the digitalinic acid is thrown down; the rest may be precipitated by boiling with sulphate of copper, and obtained in the free state by decomposing this salt with hydrosulphuric acid.

Properties. Crystalline mass consisting of microscopic, shining, and translucent plates. It has an acid reaction, and tastes somewhat bitter. When dried at 100° it contains 50·94 p. c. C., 7·54 H., and 41·52 O.

By boiling with *acids*, it is resolved into digitaliretin and sugar.

Digitalinic acid combines with *bases*. With *soda* it forms a salt, which crystallises in rosettes, and, when dried at 100°, contains on the average 14·08 p. c. soda. — It precipitates *lead* and *silver salts*.

Digitalinic acid is soluble in *alcohol*.

3. Digitalic Acid.

PYR. MORIN. *N. J. Pharm.* 7, 295.

Preparation. The hot aqueous infusion of fox-glove leaves is eva-

porated over a water-bath; alcohol of 92 p. c. is added to the syrup as long as a precipitate is formed; the liquid is filtered after some days; the alcohol distilled off the filtrate; and the remaining liquid is evaporated down to a thick extract.   This extract is digested several times in hot ether, until it has lost all bitterness, whereupon (according to Morin !) digitalin and digitalic acid are dissolved.   Caustic baryta is now gradually added to the ethereal tinctures, till they acquire an alkaline reaction ; and the yellow precipitate is collected, washed with ether till it is no longer bitter, then with alcohol of 92 p. c., as long as the alcohol becomes coloured, and decomposed under water with (preferably an insufficient quantity of) dilute sulphuric acid.   The reddish and very acid filtrate is evaporated, excluding the air as much as possible, and decanted after cooling and standing, to allow the separation of a brown flocculent precipitate; alcohol of 95 p. c. is added to precipitate any digitalate of baryta that may have remained in solution ; and the filtrate is evaporated in vacuo to the crystallising point.   The crystals found in the brown mother-liquor must be recrystallised from alcohol with the least possible access of air.

Properties.   White needles, having a not unpleasant sour taste. They redden litmus strongly, and have a faint peculiar odour.

Decompositions.   Digitalic acid, when *heated*, melts, gives off a suffocating vapour, blackens, burns with a white flame, and leaves a light inflammable charcoal. — Exposed to *light* or *air*, especially in presence of alkalis, it is changed to a black product, which then colours the solutions, and does not dissolve in water, but easily in alcohol; less in ether.

Combinations.   Digitalic acid is easily soluble in *water*.   It decomposes carbonates, displacing the carbonic acid.

Its soluble salts soon become yellow when exposed to the air. The deliquescent *potash-salt* crystallises with difficulty; the *soda-salt* better.   The *baryta* and *lime-salts* are soluble in water, insoluble in alcohol and ether.   The *magnesia-salt* is soluble in water.

Digitalate of Zinc.—When digitalic acid is agitated with excess of carbonate of zinc, an acid filtrate is formed which, on evaporation in vacuo, deposits at first a transparent gum, which, after some days, becomes crystalline.   It does not become coloured on exposure to the air so quickly as the other salts.

Digitalate of Lead is white, heavy, and insoluble ; the *copper-salt* is green, insoluble ; the *silver-salt* white, insoluble in water, soluble in nitric acid.

Digitalate of soda throws down a copious flocculent precipitate from a watery solution of *ferrous sulphate,* but does not alter ferric acetate.

Digitalic acid dissolves very easily in *alcohol,* less in *ether.*

4. Fatty Acids from Digitalis.

KOSMANN (1846). *J. Chim. méd.* 22, 377.

Digitoleic acid.

Compare Kosmann's Digitalin (p. 337).

The ethereal solutions of the acid obtained as there described leaves on evaporation a green oil, which soon solidifies into a granulo-crystalline mass. This is dissolved in an aqueous solution of bicarbonate of soda, precipitated with acetic acid, then washed, and dissolved in ether, from which it is recovered on evaporation.

Green, star-shaped groups of needles, which melt at 30°, make grease-spots on paper, have a not unpleasant odour, and sharp, bitter taste. Its alcoholic solution reddens litmus.

Sparingly soluble in *water*. — Decomposes the aqueous solutions of the *carbonates* and *bicarbonates of the alkalis*, dissolves in them, and is precipitated in green flocks by acids. — It forms with the *heavy metallic oxides*, insoluble, yellow or green feathery salts.

Potash-salt. — The acid dissolves slowly in cold aqueous solution of bicarbonate of potash. The solution is evaporated to dryness, and the residue digested in cold alcohol of 85 p. c.; this leaves on evaporation a greenish-brown imperfectly crystalline residue which does not contain any carbonate of potash. Its aqueous solution froths like soap-water.

Soda-salt. — Obtained in the same manner as the potash-salt. It is a soft soapy mass, soluble in ether.

Baryta-salt. — Obtained from the potash-salt by double decomposition. It crystallises in tufts, which at 100° become green and gummy. It contains 18·72 p. c. baryta, and 81·28 p. c. acid.

Lead-salt. — Obtained from the soda-salt and neutral acetate of lead by double decomposition. Green gummy tufts, which melt at 60°, and do not solidify in the crystalline form on cooling. It contains 25·13 p. c. oxide of lead, and 74·87 p. c. acid. On being drenched with ether, it is resolved into an acid salt which dissolves, and a residue of basic salt, the latter containing, at 100°, 64·88 p. c. oxide of lead and 35·12 acid.

The acid is easily soluble in *alcohol* and *ether*.

Primary Nucleus $C^{32}H^{32}$.

Cetylene.

$C^{32}H^{32}$.

DUMAS & PELIGOT. *Ann. Chim. Phys.* 62, 8; *Pogg.* 36, 139; *J. pr. Chem.* 9, 285.

BERTHELOT. *Compt. rend.* 44, 1350; *N. Ann. Chim. Phys.* 51, 81; *Chim. organ.* 1, 121; *Ann. Pharm.* 104, 184; *J. pr. Chem.* 72, 106; *Chem. Centr.* 1857, 573.

Cétène. Cetylen. Aethalen. (See vii, 155.)

Formation. — 1. From ethal by the action of phosphoric acid (Dumas & Peligot). — 2. Chloride of cetyl, on continued boiling, gives up hydrochloric acid, and is converted into cetylene (Tuttscheff). — 3. By the action of pentachloride of phosphorus on ethal, chloride of cetyl and cetylphosphoric acid being formed at the same time (Tuttscheff). — 4. By the dry distillation of spermaceti-fat (Smith). — 5. One of the oils resulting from the dry distillation of stearic acid is probaby cetylene (Redtenbacher).

Preparation. Ethal is distilled once or twice with pounded commercial glacial phosphoric acid, and the distillate is redistilled with anhydrous phosphoric acid (Dumas & Peligot). The distillate collected from the rapid distillation of spermaceti forms, with potash-ley, a soap from the aqueous solution of which ether extracts cetylene (Smith).

Properties. Colourless, non-solidifiable oil, which makes greasestains on paper. Boils at 275° (274°, Tuttscheff) without decomposition. Neutral, tasteless. Vapour-density = 8·007 (Dumas & Peligot). Sp. gr. 0·7893 at 15·2°, the sp. gr. of water at 4° being taken as unity (Mendelejef). (*Compt. rend.* 51, 97 ; *Kopp's Jahresb.* 1860, 7.)

					Dumas & Peligot.		Smith.
32 C	192		85·71		84·98		84·40
32 H	32		14·29		14·20		14·12
					99·18		98·52

	volumes.		density.
C-vapour	32		13·312
	32		2·218
Cetylene-vapour	2		15 530
	1		7·765

Cetylene *burns* with a pure white flame (Dumas & Peligot). It combines at ordinary temperatures and at 100° with *hydrochloric* and *hydrobromic acids*. When cetylene is heated to 100° with a large excess of a cold-saturated aqueous solution of hydrochloric acid in a sealed tube for 100 hours, about the half of the cetylene is converted into chloride of cetyl (or an isomeric compound, as shown at least in the case of the amyl series? Kr.); nevertheless, it does not appear that there is any excess of cetylene to be separated (Berthelot).

Cetylene is insoluble in *water*, but dissolves easily in *alcohol* and in *ether* (Dumas & Peligot).

Cetylic Ether.

$$C^{32}H^{33}O = C^{32}H^{32},HO.$$

More correctly $C^{64}H^{66}O^2 = C^{32}H^{33}O,C^{32}H^{33}O.$
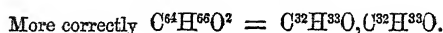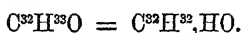
Fridau. *Ann. Pharm.* 83, 22.

Oxide of Cetyl.

Iodide of cetyl is heated to 110° with sodium-ethal till it is decomposed, with separation of iodide of sodium; the product is dissolved in ether; the iodide of sodium separated by boiling with water; and the product is finally purified by repeated crystallisation from boiling alcohol, washing, and melting the crystals in water. — When ethal is heated with oil of vitriol the mixture contains, according to Heintz, cetyl-ether and cetyl-aldehyde. See page 345.

Beautiful shining laminæ, melting at 55°, and solidifying to a radiating mass at 53·5°. At 150° it turns brown, gives off a faint, fatty odour, and a small quantity of brown distillate, the remainder passing over unchanged at about 300°.

It is decomposed by oil of vitriol, but is not changed by boiling hydrochloric or nitric acids.

				Fridau.
				mean.
32 C	192	....	82·40	82·02
33 H	33	....	14·17	14·24
O	8	....	3·43	3·74
$C^{32}H^{33}O$	233	....	100·00	100·00

Ethal.

$$C^{32}H^{34}O^2 \ = \ C^{32}H^{32},H^2O^2.$$
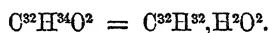
CHEVREUL. *Ann. Chim. Phys.* 7, 157.—*Recherches sur le corps gras,* 161 and 239.

LECANU & BUSSY. *J. Pharm.* 12, 625; *Mag. Pharm.* 17, 150; *Ann. Chim. Phys.* 34, 57.

DUMAS & PELIGOT. *Ann. Chim. Phys.* 62, 5; *J. pr. Chem.* 9, 285.

DUMAS & STASS. *Ann. Chim. Phys.* 73, 113; *Ann. Pharm.* 35, 139.

L. SMITH. *Ann. Pharm.* 42, 241; *N. Ann. Chim. Phys.* 6, 40.

STENHOUSE. *Phil. Mag. J.,* 20, 271; *Mem. Chem. Soc.* 1, 43; *J. pr. Chem.* 27, 253.

FRIDAU. *Ann. Pharm.* 83, 1; abstr. *J. pr. Chem.* 57, 457; *N. Ann. Chim. Phys.* 36, 365. Preliminary notice: *Ann. Pharm.* 80, 117.

W. HEINTZ. Also as a survey of the whole of Heintz's researches on the fats. — 1. Melting point of Stearin: *Berl. Akad. Ber.* 1849, 222; *J. pr. Chem.* 48, 382; *Pharm. Centr.* 1850, 188; *Inst.* 1849, 390; *Lieb. Kopp's Jahresb.* 1849, 342. — 2. Mutton-fat, Spermaceti, Human fat; *Pogg.* 84, 221 and 238; *J. pr. Chem.* 53, 443; *Ann. Pharm.* 80, 293; *Pharm. Centr.* 1851, 645; *Inst.* 1852, 63; *Lieb. Kopp's Jahresb.* 1851, 446. — 3. Spermaceti: *Pogg.* 87, 21 and 267; *J. pr. Chem.* 57, 30; *Pharm. Centr.* 1852, 583; *Chem. Gaz.* 1852, 321; *N. Ann. Chim. Phys.* 37, 361; *Lieb. Kopp's Jahresb.* 1852, 503. — 4. Mutton-fat. Mixed nature of Margaric acid: *Pogg.* 87, 553; *J. pr. Chem.* 57, 300; *Ann. Pharm.* 84, 297; *Pharm. Centr.* 1852, 777. *Chem. Gaz.* 1853, 41; *Lieb. Kopp's Jahresb.* 1852, 515.—5. Beef-suet: *Pogg.* 89, 579; *Ann. Pharm.* 88, 295; *Lieb. Kopp's Jahresb.* 1853, 445.— 6. Butter: *Pogg.* 90, 137; *Ann. Pharm.* 88, 300; *J. pr. Chem.* 60, 301; *Chem. Gaz.* 1853, 441; *N. J. Pharm.* 25, 71; *Lieb.*

Kopp's Jahresb. 1853, 447. — 7. Spermaceti : *Pogg.* 92, 429 and 588 ;
Ann. Pharm. 92, 291 ; *J. pr. Chem.* 62, 349 and 482 ; 63, 162 ; *Pharm.
Centr.* 1854, 585 ; *Phil. Mag.* (4) 9, 74 ; *Inst.* 1854, 405 ; *Lieb. Kopp's
Jahresb.* 1854, 456. — 8. Melting-point of Stearin : *Pogg.* 93, 431 ;
Ann. Pharm. 92, 300 ; *J. pr. Chem.* 63, 168 ; *Pharm. Centr.* 1854,
777 ; *Inst.* 1855, 116 ; *Chem. Gaz.* 1854, 461 ; *Lieb. Kopp's Jahresb.*
1854, 447. — 9. Action of Nitric acid on Stearin : *Pogg.* 93, 443 ;
Ann. Pharm. 92, 290 ; *J pr. Chem.* 64, 56 ; *Lieb. Kopp's Jahresb.* 1854,
446. — HEINTZ & HETZER against COLLET. Olive oil : *J. pr. Chem.*
64, 111 ; *Lieb. Kopp's Jahresb.* 1854, 461. — 11. Action of Potash-
lime on Ethal : *Pogg.* 93, 519 ; *Ann. Pharm.* 92, 299 ; *J. pr. Chem.* 63,
364 ; *Pharm. Centr.* 1854, 907 ; *Lieb. Kopp's Jahresb.* 1854, 460. —
12. Against Scharling : *Ann. Pharm.* 97, 271 ; *Lieb. Kopp's Jahresb.*
1855, 616. — 13. Distillation of Stearin : *Pogg.* 94, 272 ; *J. pr. Chem.*
64, 413 ; *Pharm. Centr.* 1855, 174 ; *Inst.* 1855, 235 ; *Lieb. Kopp's
Jahresb.* 1855, 514. — 14. Distillation of Stearate of Lime : *Pogg.* 96,
65 ; *J. pr. Chem.* 66, 121 ; *Pharm. Centr.* 1855, 591 ; *Inst.* 1855, 432 ;
Lieb. Kopp's Jahresb. 1855, 516. — 15. Olive oil : *J. pr. Chem.* 70, 366 ;
Pharm. Centr. 1857, 735 ; *Kopp's Jahresb.* 1857, 353. — 16. Com-
binations of Cetyl; Artificial Margaric acid : *Pogg.* 102, 257 ;
J. pr. Chem. 72, 173 ; *Chem. Centr.* 1857, 684 ; *Kopp's Jahresb.* 1857,
355 and 445. — Summary of 1 to 14 : *J. pr. Chem.* 66, 1.

BECKER. *Ann. Pharm.* 102, 209 ; *J. pr. Chem.* 72, 126 ; *Chem. Centr.*
1857, 486 ; *N. Ann. Chim. Phys.* 52, 340 ; *Kopp's Jahresb.* 1857,
355.

BERTHELOT. *Compt. rend.* 44, 1350 ; *N. Ann. Chim. Phys.* 51, 81 ; *N. J.
Pharm.* 32, 90 ; *J. pr. Chem.* 72, 106 ; *Ann. Pharm.* 104, 184 ; *Chem.
Centr.* 1857, 573 ; *Kopp's Jahresb.* 1857, 425. — *Compt. rend.* 47, 262 ;
N. Ann. Chim. Phys. 56, 51 ; *Ann. Pharm.* 112, 356 ; *Kopp's Jahresb.*
1858, 417.

TUTTSCHEFF. *Zeitschr. Chem. Pharm.* 4, 59 ; *Kopp's Jahresb.* 1860, 405.

Cetylalcohol. — First described by Chevreul in 1818. Occurs in
spermaceti, combined with different fatty acids in the form of an
ether.

Preparation.   1. Spermaceti is saponified as described at page 45,
vol. xv, with alcoholic potash, and the fatty acids are separated as
baryta-salts, in the manner there described, from the ethal, which
remains dissolved in ether. The ether is distilled off from the ethereal
solution of the ethal ; the residue is boiled for some time with dilute
hydrochloric acid, to remove any baryta that may remain, then dis-
solved in warm alcohol ; and the ethal which crystallises out on con-
centrating and cooling the liquid is purified by repeated pressure
and recrystallisation from alcohol. Small portions of spermaceti which
have escaped saponification separate on gradual cooling from the
alcoholic solution, if not too concentrated, so that the ethal-solution can
be poured off from them, and that which then crystallises out may be
brought to the melting point of 49° to 49·5° (Heintz). Or the ethal
which first separates may be boiled with additional alcoholic potash to
ensure the decomposition of the whole of the spermaceti (Heintz,
Becker). — 2. Spermaceti is melted with half its weight of hydrate of
  a, the temperature not being allowed to rise above 110° to 120° ;
   is treated with boiling aqueous hydrochloric acid ; the floating

oily mixture of fatty acids and ethal is again melted with potash ; the whole is suspended in hot water, and precipitated by chloride of calcium, and the precipitate is collected and dried. The ethal is separated from the lime-soap by hot alcohol or ether, as in 1 (Dumas and Peligot, Smith). Fridau uses, instead of the solid hydrate, a solution of potash, strong enough to solidify when cold. Chevreul saponifies with strong aqueous potash-ley, in which case, however, the mixture must be heated for several days. The ethal has still to be purified by distillation (Dumas & Peligot).

The ethal obtained in this manner is not the pure compound $C^{32}H^{34}O^2$, but contains in addition to this, which is its chief constituent, small quantities of stethal, $C^{36}H^{38}O^2$, methal (p. 209), and lethal (xv. 43) alcohols which are far from having been completely isolated and obtained in a state of purity. Their presence is manifested by the behaviour of the ethal with hydrate of potash, as described at page 346. If the ethal is recrystallised several times from alcohol until its melting point is brought to 49°, a portion of the ethal, together with the whole or nearly the whole of the methal and lethal, remains in the mother-liquor, while the portion which crystallises out contains the stethal together with ethal (Heintz).

Properties. Ethal, when melted and gradually cooled, crystallises in shining laminæ ; from a hot alcoholic solution it separates in small spangles, which glitter less than those of spermaceti. Colourless, translucent. Melts above 48° (Chevreul), at 48·3° (Stenhouse), at 49·5° (Heintz), and solidifies at 48°. It evaporates even when spermaceti is boiled with potash-ley, so that a funnel held over the mass becomes covered with it ; it likewise evaporates completely when heated in an open dish (Chevreul), and passes over quite undecomposed on repeated distillation (Bussy & Lecanu). — Boiling point about 400° (Dumas & Peligot). Without taste or smell ; neutral. — For its specific heat, the latent heat of its vapour, and latent heat when melted, see Favre & Silbermann. (*N. Ann. Chim. Phys.* 37, 461.)

		Chevreul.	Dumas & Peligot.	Stenhouse.	Heintz.
32 C	192	79·34	78·68	78·10	78·22	79·27
34 H	34	14·05	13·95	14·24	13·96	14·06
2 O	16	6·61	7·37	7·66	7·82	6·67
$C^{32}H^{34}O^2$	242	100·00	100·00	100 00	100·00	100·00

It must be regarded as an alcohol (vii. 191).

Decompositions. 1. When the vapour of ethal is passed through a *red-hot* tube, gaseous and liquid hydrocarbons are formed, containing equal numbers of atoms of hydrogen and carbon ; among them propylene C^6H^6 occurs in large quantity (Cahours, *Compt. rend.* 32, 142). — 2. When heated in the air, it *burns* like wax (Chevreul). — 3. By repeated distillation with anhydrous *phosphoric acid*, it is converted into cetylene (p. 341) (Dumas & Peligot). — 4. When *hydrochloric acid* is passed through melted ethal, or through its solution in absolute alcohol, the melting point is but little altered, and no chloride of cetyl is produced (Heintz). — 5. When ethal is boiled with 100 parts of *nitric acid* of sp. gr. 1·28, a large quantity of nitrous acid is given off, and by repeated cohobation, till the residue becomes soluble in the distillate, a crystallisable acid body is formed, which does not precipi-

ta'e lime-water (Chevreul). — 6. Ethal heated with *bichromate of potash* and dilute sulphuric acid yields cetylic aldehyde (Fridau).

7. It is not altered by cold *oil of vitriol*, but, on being heated with it, is converted into cetylsulphuric acid. It is carbonised by distillation with oil of vitriol (Dumas & Peligot).

Ethal mixed with 10 parts of oil of vitriol at 18° assumes in two hours a pale reddish-yellow colour, and gives off a little sulphurous acid; at 100° it changes to a full brown-red, gives off much sulphurous acid, and is then but sparingly soluble, with diminished colour, in the acid; above 100° it is blackened without being dissolved, and appears to give off hydrosulphuric acid (Chevreul). With melted ethal, even cold sulphuric acid produces cetylene-sulphuric acid, but when ethal is heated in a water-bath, out of contact of air with half its weight of oil of vitriol, sulphurous acid is given off, and a dark brown mass is formed, containing scarcely any cetylene-sulphuric acid, but a body which is insoluble in alcohol, and solidifies on cooling. After being crystallised eight times from ether, with the help of animal charcoal, it melts at 53·4°, but the melting point is still not quite constant. It contains, on the average, 81·40 p. c. C., 13·84 H., and 4·76 O., so that it is probably a mixture of cetylic ether and cetylic aldehyde, like that which is formed in the preparation of cyanide cetyl and of artificial margaric acid (Heintz). The same mixture is formed when ethal is heated with excess of common salt and a quantity of oil of vitriol not sufficient to decompose the whole, and may be extracted from the mass by boiling ether. After 13 crystallisations from ether-alcohol, its melting point is raised from 47·9° to 55·7°. The substance melting at 53° contains 81·24 C., 13.75 H., and 5·01 O. (Heintz).

8. By *iodine* and *phosphorus*, ethal is converted into iodide of cetyl; by *bromine* and *phosphorus*, into bromide of cetyl.

9. With *pentachloride of phosphorus* ethal becomes heated, gives off a large quantity of hydrochloric gas, and forms chlorophosphoric acid and chloride of cetyl (Dumas & Peligot) together with cetylene and cetyl-phosphoric acid, which is left in the residue (Tuttscheff).

10. Ethal heated with 5 or 6 parts of *potash-lime* to 210° or 220° gives off hydrogen, and forms palmitate of potash (Dumas and Stas).

$$C^{32}H^{34}O^2 + KO,HO = C^{32}H^{31}KO^4 + 4H.$$
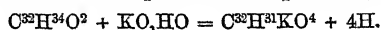
The evolution of hydrogen does not become rapid till the mixture is heated to between 263° and 275°; the resulting acid is a mixture containing a considerable quantity of palmitic acid, together with stearic, myristic, and lauric acids. The last three acids are formed from stethal, methal, and lethal—compounds which cannot themselves be separated from ethal—in the same way as palmitic acid is formed from ethal properly so called (Heintz). Scharling (*Ann. Pharm.* 96, 236) likewise found butyric acid in the residue obtained after heating ethal with potash-lime; but according to Heintz, this acid is present only when the air has had access to the mixture.

11. *Potassium* or *sodium* disengages hydrogen from melted ethal, and forms potassium-ethal or sodium-ethal, compounds in which 1 at. hydrogen is displaced by 1 at. metal; they are decomposed by the action of dilute hydrochloric acid, into chloride of sodium and

ethal (Löwig, *Pogg.* 43, 622), (Fridau). Sodium-ethal obtained at 110° is solid, yellowish-grey, and melts partially at 100°, completely at 110°. It is not altered by boiling water (Fridau).

12. By the action of *sulphide of carbon* and *hydrate of potash*, ethal is converted into cetylxanthate of potash (Provostaye & Desains).

13. From the *organic acids* and ethal the cetylic ethers are formed, with elimination of water. Those containing acetic, butyric, benzoic, and stearic acids are formed by heating these acids with ethal to 200° (Berthelot). Ethal heated with succinic acid yields succinate of cetyl, but no corresponding compound is obtained by heating ethal with oxalic acid (Tuttscheff). Acetate of cetyl is formed by the aid of sulphuric or hydrochloric acids in a mixture of ethal and acetic acid; benzoate of ethal is formed from ethal and chloride of benzoyl (Becker). When ethal is heated to 100° for 9 hours with an equivalent quantity of acetic acid, 38·7 p. c. of the ethal enters into combination; if for 40 hours. 63·7 p. c.; while if, instead of ethal, common alcohol is used, from 41·2 to 59·8 p. c. of it is converted into ethylic acetate (Berthelot & Péan de St. Gilles, *Compt. rend.* 55, 43).

14. Ethal combined with sodium is attacked by *chloroform* and by *chloride of ethylene* (oil of olefiant gas, viii, 376), (Tuttscheff); by *hydriodate of aniline* at 120°, it is decomposed into chloride of sodium and crystals which melt less easily than ethal, but dissolve more freely in alcohol; heated with *iodide of cetyl*, it yields cetylic ether (Fridau).

Combinations. Ethal is not soluble in *water*, and is not altered by boiling with water (Chevreul).

It forms a crystallisable compound with *bichloride of tin* (Lewy, *Compt. rend.* 21, 371).

Ethal dissolves in all proportions in *alcohol* of sp. gr. 0·812 at 54°, and crystallises in part on cooling. — It dissolves freely in *ether*. — It mixes with *fatty acids.* 60 parts of a mixture of margaric and oleic acids, melting at 45°, yield, on addition of 40 parts ethal, a mixture melting at 43° to 44° (Chevreul).

Appendix to Ethal.

Cetin or Spermaceti-fat.

Spermaceti is found in peculiar cavities in the head of *Physeter macrocephalus, Ph. Tursio* and others, and of *Delphinus edentulus,* being kept in solution in the sperm-oil by the heat of the animal's body, and crystallising out after death. It is freed as much as possible from oil by filtration and by treatment with potash-ley, and then melted. The fused and solidified mass, constituting the spermaceti of commerce, is white, scaly, brittle, soft to the touch, of sp. gr. 0·943 at 15° (0·843 at 50°, 0·824 at 81°, 0·813 at 94°, the sp. gr. of water at 15° being taken at 1), (Saussure); melting point from 38° to 47°; nearly tasteless, inodorous, and neutral.

Spermaceti is also found in small quantity in the blubber of the *Balaena rostrata* (Scharling, *J. pr. Chem.* 43, 257), and, with but slightly different properties, in the oil of *Delphinus globiceps* (Chevreul).

When spermaceti is freed from adhering sperm-oil by means of cold alcohol, and the residue repeatedly crystallised from hot alcohol, the *spermaceti-fat* or *cetin* of Chevreul is obtained. This may be still further purified by crystallisation from boiling ether (Heintz, Hofstädter).

Properties of Cetin. Soft white laminæ having a pearly lustre melts at 49° (Chevreul), 53·5° (Heintz), 54·5° (Hofstädter), and solidifies at 48·4° to 49·4° (Stenhouse), 50·5 (Hofstädter), to a compact radiate mass. If not exposed to the air, it evaporates without decomposition at a temperature near 360° (see below). — Inodorous; neutral (Chevreul). Cetin crystallised from dolphin oil, and purified by alcohol, solidifies partly at 45°, wholly at 43·5° (Chevreul).

				Chevreul.		Smith.		Stenhouse.		Heintz.
64 C	384	....	80·00	....	80·0	....	79·71	....	78·66	....	80·03
64 H	64	....	13·33	....	12·8	....	13·30	....	13·21	....	13·25
4 O	32	....	6·67	....	7·2	....	6·99	.	8·13	....	6·72
$C^{64}H^{64}O^4$	480	....	100·00	....	100·0	....	100 00	....	100·00	....	100·00

Cetin is formed from palmitic acid and ethal, with elimination of water, and may be separated into these compounds, with assumption of water (L. Smith): it may therefore be regarded as palmitate of cetyl. Spermaceti yields by saponification, besides palmitic acid, small quantities of stearic, myristic, and lauric acids, and, besides ethal, also stethal, methal and lethal, which acids and alcohols are present in the form of compounds analogous to palmitate of cetyl (Heintz). — The ethereal nature of spermaceti was first recognised by Chevreul, more exactly by Dumas & Peligot, the former of whom regarded the acids obtained by saponification of spermaceti as oleic and margaric acids.

Decompositions. · 1. By *dry distillation* a distillate is obtained, which has a lower melting point (23·5° Chevreul, 23° Bussy & Lecanu), does not yield sebacic acid to water (whence it follows that cetin contains no oleic acid: *Stenhouse*), and may be saponified by potash. From this soap-ley, ether extracts an oil, probably cetylene, and perhaps some undecomposed spermaceti; the soap contains palmitic acid (melting at 55°) and one of the liquid acids derived from the sperm oil. Moreover, towards the end of the distillation, water, carbonic acid, carbonic oxide, and olefiant gas pass over, while charcoal remains. No ethal is formed in this decomposition (L. Smith). Bussy & Lecanu obtained also acetic acid and a yellow material resembling camphor, perhaps chrysene (xv. 1). — 2. Spermaceti *burns* with a bright flame like wax. — 3. It is decomposed by superheated *steam* at 160°, in the same manner as by strong bases (Scharling).

4. When cetin is heated with *nitric acid*, nitrous fumes are slowly given off; but even after 3 or 4 days, some of the fat, having a rancid smell, still floats in the acid; in fact 10 days' digestion, with addition of fresh acid, is required to dissolve it, and from 15 to 20 days to oxidise it completely (Smith). After 24 hours' action of the acid, the cetin becomes soft, crystalline, and easily soluble in potash-ley; from the alkaline solution, mineral acids separate a solid and an oily acid (Radcliff, *Ann. Pharm.* 43, 349). By this oxidation there are formed: a. *Oenanthylic acid* (xii, 451), as a volatile oil floating in the distillate (Radcliff, Arppe). — b. *Succinic acid* (Chevreul), confirmed by Radcliff and Arppe. — c. According to Smith, *adipic acid,* which was

not found either by Radcliff or by Arppe, and is regarded by the latter, not as a distinct compound, but as a mixture of succinic acid with more easily fusible acids. — A. *Pimelic acid* (xii, 463), according to Radcliff. Arppe formerly also doubted whether this was a distinct acid (*Ann. Pharm.* 115, 143), but afterwards (*Ann. Pharm.* 124, 98), he acknowledged it to be so.   Arppe (*Ann. Pharm.* 120, 292 ; 124, 98), by boiling spermaceti in a retort for 10 hours with 2 parts nitric acid of sp. gr. 1·25, pouring back the distillate, removing the acid solution, pouring on fresh acid, and continuing this treatment for 8 or 10 days, obtained, besides volatile oenanthylic acid, a non-volatile oil, which solidified with difficulty in the cold, and an acid solution from which he separated succinic, suberic, pimelic (see on this, Arppe's more recent statement ; *Ann. Pharm.* 124, 98), and sebacic acids.   See also below, the decomposition of oleic acid by nitric acid.

5. Cetin digested with 10 parts oil of vitriol dissolves in a few hours to a thick yellow liquid, which on standing separates into two layers, and when heated gives off sulphurous acid, perhaps also hydrosulphuric acid, and chars (Chevreul). — 6. Cetin is saponified by aqueous solution of *potash* much less quickly than tallow, but more quickly by alcoholic potash, or by the fused hydrate, yielding the product above described (p. 348).   If it be too strongly heated with hydrate of potash, the hydrogen required for the formation of ethal is given off (Gerhardt, *Précis*, 1, 131) :

$$C^{64}H^{64}O^4 + 2(KO,HO) = 2C^{32}H^{31}KO^4 + 4H.$$
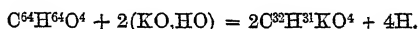
Cetin from dolphin-oil saponifies more readily, yielding more fatty acid and less ethal than the ordinary variety (Chevreul). — Respecting the adulterations of spermaceti and their detection, see Chateau (*Mulh. Soc. Bull.* 32, 415).

Cetin is not soluble in liquid *carbonic acid* (Gore). — It dissolves in 6·33 parts of boiling *alcohol* of sp. gr. 0·791, in 40 parts alcohol of sp. gr. 0·821 (according to a later account in 33 parts of sp. gr. 0·834), and the greater part crystallising out on cooling (Chevreul).   It dissolves completely in cold *ether*, and so copiously in hot ether that the solution becomes solid in cooling.   It is soluble in warm *wood-spirit*, and in *oils* both *fixed* and volatile.

Cetylic Aldehyde.

$$C^{32}H^{32}O^2 = C^{32}H^{32},O^2.$$
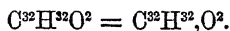
FRIDAU.   *Ann. Pharm.* 83, 23.

Palmitic aldehyde.

A mixture of ethal and bichromate of potash is heated with dilute sulphuric acid till the ethal melts, and the mass blackens with brisk effervescence.   As soon as the action ceases, the mass is again warmed, then boiled repeatedly with water ; and the undissolved fatty substance is purified by repeated crystallisation from weak and strong alcohol, ether, ether-alcohol, and at last from boiling alcohol.   The crystals are boiled with water, then melted and filtered through cotton-wool. At a higher temperature, or with concentrated sulphuric acid, a dark-coloured resin

is obtained, which is not easily purified. The yield is very small. When ethal is heated with oil of vitriol, a mixture of cetylic aldehyde and cetylic ether is obtained (Heintz). See page 346.

Fine colourless crystals. Melts at 52°, and solidifies at 50° to a radiate mass. Turns brown at 160°. Very slightly volatile.

Fridau.

32 C	192		80·00		19·55
32 H	32		13·33		13·24
2 O	16		6·67		7·21
C³²H³²O²	240		100·00		100·00

Cetylic aldehyde does not combine with *ammonia*, with *aniline*, or with the *bisulphites of the alkalis* (Limpricht, *Ann. Pharm.* 94, 246).

Palmitic Acid.

$$C^{32}H^{32}O^4 = C^{52}H^{32},O^4.$$
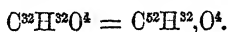
CHEVREUL.   *Recherches sur les corps gras*, 59.
DUMAS & STRASS.   *Ann. Chim. Phys.* 73, 113; *Ann. Pharm.* 35, 139.
VARRENTRAPP.   *Ann. Pharm.* 35, 209.
FRÉMY.   *Ann. Pharm.* 36, 44.
STENHOUSE.   *Ann. Pharm.* 36, 50; *Phil. Mag. J.* 18, 186.
L. SMITH.   *Ann. Pharm.* 42, 241; *N. Ann. Chim. Phys.* 6, 40.
B. STHAMER (& MEYER).   *Ann. Pharm.* 43, 335.
H. SCHWARTZ.   *Ann. Pharm.* 60, 69.
HEINTZ.   In the places above referred to (pp. 343, 344).
V. BOECK.   *J. pr. Chem.* 49, 295; *Pharm. Centr.* 1850, 555; *Chem. Gaz.* 1850, 309; *Lieb. Kopp's Jahresb.* 1850, 404.
BERTHELOT.   1. Glycerides: *Compt. rend.* 36, 27; *N. J. Pharm.* 23, 410; *J. pr. Chem.* 58, 412; *Compt. rend.* 37, 398; *N. J. Pharm.* 24, 259; *J. pr. Chem.* 60, 193; *Ann. Pharm.* 88, 304; *Chem. Soc. Qu. J.* 6, 280; in detail, *N. Ann. Chim. Phys.* 41, 216; abstr. *J. pr. Chem.* 62, 451. — 2. Formation of Ethers: *Compt. rend.* 37, 885; *J. pr. Chem.* 61, 156; *Ann. Pharm.* 88, 312; *Pharm. Centr.* 1854, 43; in detail, *N. Ann. Chim. Phys.* 41, 432. — 3. Mannitanides: *Compt. rend.* 41, 452; *J. pr. Chem.* 67, 235; in detail, *N. Ann. Chim. Phys.* 47, 297.
MASKELYNE.   *Chem. Soc. Qu. J.* 8, 1; *J. pr. Chem.* 65, 287; *Pharm. Centr.* 1855, 417.

History.   (See vii. 237—239.)   Chevreul in 1820 distinguished the solid acids resulting from the saponification of fats as *margaric acid* and *margarous*, afterwards *stearic acid*, the former melting at 60°, the latter at 75°, and solidifying at 70°. He did not consider the difference between the two acids to be fully established, but suggested that margaric acid might be a mixture of stearic acid with another acid more easily fusible and richer in oxygen. According to Chevreul, acids with irregular melting-point were often associated with margaric acid, to which the formula $C^{34}H^{34}O^4$ was then assigned; on the other hand, palmitic acid, and many mixtures of palmitic or stearic acid with

other acids, received peculiar names. Heintz, in 1852 and afterwards, showed that :

1. All the acids obtained in the saponification of fats contain a number of carbon-atoms divisible by 4 without remainder.

2. The margaric acid of most chemists is separable into palmitic and stearic acids.

3. Fatty acids may be mixtures and not definite compounds, even though neither their composition nor their melting point can be altered by recrystallisation.

4. Such mixtures may, however, be separated by partial precipitation (xvi. 210).

5. They differ from pure acids as regards their melting-point and their mode of solidifying.

Heintz has, moreover, the merit of having determined with accuracy the melting-point, composition, and many other properties of the fatty acids, and also of having drawn up the tables hereafter to be given of mixtures of fatty acids of known composition. From these, and the investigations of other chemists subsequently published, it appears that the nature of the bodies described as margaric acid is probably as follows :—

a. Margaric acid of Chevreul. This, according to Heintz, is to be regarded as a mixture of about 90 p. c. palmitic acid and 10 p. c. stearic acid, which is probable from the circumstance that it crystallises in needles on cooling. Of similar nature are doubtless the margaric acid of Varrentrapp (*Ann. Pharm.* 35, 84), obtained from human fat; that from goose-fat by Gottlieb (*Ann. Pharm.* 57, 36); from shea-butter by Thomson & Wood (*J. pr. Chem.* 47, 237), and many others.

b. Margaric acid of Bromeis. The acid obtained by oxidation of stearic acid is undecomposed stearic acid, which owes its lower melting-point to association with volatile acids (See *Stearic acid, Decomposition by Nitric acid.*) — Respecting the margaric acid which Bromeis (*Ann. Pharm.* 35, 93) obtained from impure oleic acid by the action of nitric acid, see *Oleic acid.*

c. Margaric acid of Redtenbacher and Varrentrapp. That of Redtenbacher is obtained by the dry distillation of stearic acid, when, according to Heintz, most of the stearic acid passes over unchanged. That of Varrentrapp (*Ann. Pharm.* 35, 65), obtained by the dry distillation of beef-suet, hog's lard, olive-oil, or crude oleic acid, doubtless varies in composition according to the kind of fat employed; nevertheless, in those cases where 35 p. c. margaric acid were obtained by the rapid distillation of olive-oil or of crude oleic acid (*Ann. Pharm.* 45, 127), it appears certain that a decomposition of the oleic acid must have taken place, attended with formation of palmitic acid (Kr.).

d. Anderson's *Margaric acid* (*Ann. Pharm.* 63, 376) is obtained, together with hydrosulphuric acid, odmyl, and other products, by the dry distillation of almond-oil with sulphur (v. 250). It contains, on the average, 75·34 p. c. C., 12·58 H.; in the silver-salt, 28·62 p. c. silver; in the ethylic ether, 76·33 p. c. C., 12·73 H., and 10·97 O. It appears to be palmitic acid formed by the decomposition of oleic acid (Kr.).

e. Margaric acid of Poleck, Lewy, and others, obtained by the dry distillation or saponification of wax. It is doubtless palmitic acid more or less pure. (See *Cerotic acid* C⁵⁴H⁵⁴O⁴ and *Myricin* C⁶⁰.)

Occurrence of Palmitic acid. This acid is universally distributed in the fats of the animal and vegetable kingdoms. *a.* Combined with glycerin, abundantly in palm-oil (Fremy); in the Chinese tallow of *Stillingia sebifera* (Maskelyne); in Japanese wax (Sthamer); in the wax of *Myrica cerifera* (Moore). — *b.* Combined with ethal in spermaceti (L. Smith). — *c.* In the melissin of bees' wax, combined with melissylic alcohol, as palmitate of melissyl, C⁶⁰H⁶¹O,C³²H³¹O³ (Brodie, *Ann. Pharm.* 71, 144). — In changed fats, partly in the free state, especially in palm-oil.

Grain fusel-oil (*i.e.,* the greasy oil which, in the manufacture of brandy, remains upon the woollen cloth through which the brandy is filtered as it runs from the condenser) consists for the most part of margaric acid (melting point, 60°; the acid contains 74 8 C, 12 5 H.; the lead-salt, 54·2 C., 8 8 H., and 30 1 PbO.) (Kolbe, *Ann. Pharm.* 41, 53). In the fusel-oil of barley-brandy an acid occurs which resembles palmitic acid, has the same melting point, and contains 74·96 p. c. C., and 12·47 H.; the same fusel-oil appears to contain the ethylic ether of this acid (Glassford, *Ann. Pharm.* 54, 108). In both cases palmitic acid was doubtless present; Mulder (*Lieb. Kopp's Jahresb.* 1858, 302) afterwards found it also in rum fusel-oil.

Chevreul's *margaric acid* is formed in large quantities in the saponification of spermaceti of human, jaguar, and goose fats, and of dolphin and train oils; it is produced in smaller quantity, together with much stearic acid, by the saponification of butter, hog's lard, and beef and mutton suet.

Formation. 1. By the decomposition of palmitin, spermaceti, or melissin. — 2. By heating ethal with potash-lime (Dumas & Stass) p. 346. — 3. On melting oleic acid with excess of potash-hydrate, palmitic and acetic acids are produced (Varrentrapp):

$$C^{36}H^{34}O^4 + 2(KO,HO) = C^{32}H^{31}KO^4 + C^4H^3KO^4 + 2H.$$
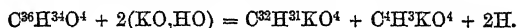
Elaidic acid behaves in the same manner (H. Meyer).

A similar formation of palmitic acid from oleic acid may take place under the following circumstances.

a. When fats or fatty substances lie for a long time in moist earth; and generally when fatty bodies are long preserved in moist places, without exposure to the air, they become harder, and resemble stearin in appearance and composition, as would be the case either on the disappearance of their olein, or on the conversion of the olein into palmitin, stearin or the corresponding acids. See *Corpse-fat* (below). The following observations seem also to belong to this place. Mutton suet is softer and yields oleic acid more readily in the fresh state than when old. Melted tallow, which had been kept for 10 years, with imperfect access of air, in a soap-factory, had become hard, very brittle, and friable. Washers soaked in tallow, used in the connections of water-pipes, had become hard after long use; the tallow obtained from them melted at 50°. A piece of tallow from a miner's lamp, which had lain in the mine for many years, was white, light, brittle,

and easily powdered, it had a sp. gr. of 0·724, melted at 59°, and contained on the average 76·02 p. c. C., 12·57 H., and 11·41 O., nearly corresponding to the composition of stearin (or palmitin, Kr.), which it resembles in its other properties. By saponification and decomposition of the soap, it yielded an acid melting at 60°. A second piece of tallow, from a similar source, but perhaps still older, contained 18 p. c. of a fat resembling stearin, and 82 p. c. of a lime-soap, the acid of which melted at 58° (Beetz, *Pogg.* 59, 111; *Ann. Pharm.* 47, 225; *Phil. Mag. J.* 23, 505; *Mem. Chem. Soc. Lond.* 1, 233).

b. When castor-oil is distilled with an excess of alkali, there remains in the residue, together with sebacic acid, an oily acid from which a large quantity of a solid fatty acid separates on standing. This fatty acid, after purification, melts at 62°, and contains 75·05 p. c. C., 12·65 H.; the ethyl-compound, which solidifies at 29·5°, contains 75·91 p. c. C., and 12·70 H. (Bouis, *N. Ann. Chim. Phys.* 44, 110). Bouis regards this substance as palmitic acid, the ethyl-compound of which, however, melts at 24·2°.

Preparation. A. *From Palm-oil.* Palm-oil is saponified with caustic potash; the soap thus obtained is decomposed; and the separated fatty acid is purified by crystallisation from alcohol (Frémy). Stenhouse dissolves the 6 or 8 times crystallised acid in caustic potash, and precipitates it with an acid. Schwarz saponifies palm-oil with caustic potash, dissolves the soap in hot alcohol, allows the solution to cool, and purifies the crystalline nodules which separate, by repeated crystallisation from alcohol, with the help of animal charcoal. The crystals, when decomposed with hydrochloric acid, yield palmitic acid, which must again be crystallised from alcohol.

B. *From Japan wax.* The wax is saponified by fusing it with half its weight of hydrate of potash, and the soap is dissolved in water and salted out. The soda-soap thus formed is dissolved in warm water and allowed to cool; it is then pressed, again dissolved in water, and the solution is heated to the boiling point, and decomposed with chloride of calcium. The lime-soap, after being washed and dried, is freed from unsaponified wax by means of ether, and decomposed by hydrochloric acid. The separated fatty acid is crystallised first from alcohol, afterwards from a mixture of alcohol and ether, and is lastly washed with cold alcohol (Sthamer).

C. *From Chinese wax.* The wax is saponified with alcoholic potash; after addition of water, the alcohol is distilled off, and the soap is decomposed with sulphuric acid. The separated fatty acid is then strongly pressed, and the press-cake is moistened with alcohol and again pressed several times. The remaining mass is crystallised from hot alcohol, until it exhibits the melting point of palmitic acid (Maskelyne).

Rochleder (*Ann. Pharm.* 50, 228) obtains palmitic acid from *coffee-beans* by the following method:—The powdered beans are extracted with ether containing water, and the ether is evaporated; the remaining yellow bitter fat is freed from the various acids of coffee, and from caffeine by shaking it repeatedly with ⅕th its volume of water and drawing off the aqueous layer of liquid, and is afterwards

saponified with caustic potash. The soap is salted out, dissolved in water, and decomposed with dilute sulphuric acid; and the mixture of oleic and palmitic acids is converted into lead-salts by boiling the acids with carbonate of soda, dissolving the soda-soap in alcohol, and precipitating with neutral acetate of lead. The lead-salts are boiled with alcohol, which dissolves them completely; but on cooling and partly evaporating the solution, the palmitate of lead separates in the form of a white powder, whilst the oleate remains in solution. The former is collected, washed with alcohol containing water, and decomposed with hydrosulphuric acid under ether-alcohol. The palmitic acid remaining behind when the filtrate is evaporated, is obtained with a melting-point of 58·5° by five times repeated crystallisation (Rochleder).

D. *From Oleic acid.* Oleic acid is saponified by a slight excess of hydrate of potash, with addition of a little water; a quantity of hydrate of potash equal to twice the weight of the oleic acid is then added, and the mixture is heated, with constant stirring, until the potash is melted, too great a heat being prevented by the occasional addition of a few drops of water, so that the mass may not blacken, but only assume a brown-yellow colour. As soon as the potash is melted, and hydrogen gas is evolved, the fire is removed, and the mass is thrown into not too large a quantity of water, when the soap which has been formed separates and floats on the surface. The soap is removed, dissolved several times in water and salted out, and afterwards decomposed with dilute hydrochloric acid; and the palmitic acid thus separated is purified by crystallisation from alcohol (Varrentrapp).

E. *From Ethal.* Ethal, mixed with five or six parts of potash-lime, is heated to 210°— 220° (263°— 275°, according to Heintz), in a metal-bath for five or six hours, or so long as hydrogen is evolved; the residue is suspended in water; and an excess of hydrochloric acid is added thereto, whereby the palmitic acid is separated in white flocks. After allowing the mixture to boil, the acid is washed, then boiled for half an hour with excess of hydrate of baryta, and evaporated to dryness. The ethal remaining undecomposed is taken up by ether; the residue is decomposed by hot hydrochloric acid; and the separated acid is washed and dissolved in ether to remove traces of undecomposed baryta-salt (Dumas & Stass). The palmitic acid thus obtained requires still to be freed from stearic, myristic, and lauric acids, which are produced at the same time (Heintz). See p. 346 and below. The fatty acids obtained by saponifying fats, or by heating with potash-lime and decomposing the soaps (and freed from oleic acid by the method given at p. 46, vol. xv.) admit of separation into two distinct portions, inasmuch as when they are dissolved in hot alcohol, a mixture of the more difficultly fusible acids containing a high percentage of carbon, especially palmitic, stearic,—and likewise arachidic acid, if present,—crystallises out on cooling; and by pressing the crystals, moistening with alcohol, and again pressing, may be obtained separately, while a smaller portion of these acids, together with the more easily fusible myristic and lauric acids, remains in solution. The acids remaining in solution are separated by methods already described (xv, 45, and xvi. 200).

When the fats contain no acids with a higher percentage of carbon

than palmitic acid, and more especially no stearic or arachidic acid, or only very small quantities thereof, they may be crystallised from alcohol, until the crystals melt at 62°, and are then to be examined as to their purity by the method given on page 210. In the contrary case, the whole of the acids are dissolved in such a quantity of alcohol, that nothing crystallises out on cooling; the solution is precipitated two or three times with a quantity of acetate of magnesia equal to about $\frac{1}{30}$th of the fatty acids; and the several successive precipitates are separated by filtering and pressing. These precipitates contain the whole of the stearic acid, provided the fat does not contain too large a quantity thereof, together with a relatively small quantity of palmitic acid. The mother-liquors diluted with a large quantity of hot water, throw down, on cooling, the palmitic acid, which is collected, examined as to its purity, and purified either by recrystallisation from alcohol, or by again precipitating it with small portions of acetate of magnesia. See page 211 (Heintz). In a later process Heintz precipitates the soda-salt, instead of the alcoholic acid, with acetate of magnesia, in the manner above described.

Older methods of preparation. 1. Chevreul's *Margaric acid.* The potash-soap of human fat, in as dry a state as possible, is digested for 24 hours with twice its weight of alcohol of sp. gr. 0 821; the undissolved portion is washed with cold alcohol and dissolved in 2 parts of hot alcohol; the solution is cooled, and the resulting mass of crystals separated from the mother-liquor; and the process of dissolving, cooling, and separating the crystals is repeated until the salt which crystallises out yields an acid melting at 60°. The mother-liquor contains a further quantity of the acid (Chevreul).

2. *Chevreul's method of preparing Stearic, Margaric and Oleic acids.* For the preparation of stearic acid Chevreul, prefers to employ mutton-suet; for the preparation of margaric acid he uses human fat. — Four parts of the fat are heated to 100° with 1 pt. of hydrate of potash and 4 pts. water (with addition of water to compensate for loss by evaporation) until the mass becomes homogeneous and pellucid, and forms a clear solution with water. It is then diluted with so much water that the solution at 50° is no longer ropy, and decomposed with an exactly equivalent quantity of phosphoric or tartaric acid. The mixture of stearic, margaric, and oleic acids which floats on the surface is allowed to solidify; the aqueous liquid is poured away; and the acids are washed repeatedly with water, and afterwards heated with 6 pts. of water, to which caustic potash is added, till complete solution is effected. This solution is poured into a quantity of water equal to 45 times the amount of the mixed acids, and left to itself at a temperature of 12°, so long as a precipitate of bi-acid stearate of potash (with which a little bi-margarate and oleate are mixed) continues to form. The liquid is decanted; the precipitate is collected on a filter and washed; the wash-water is evaporated down, mixed with the decanted liquid and again concentrated; the greater part of the potash which is now in excess, is neutralised with tartaric acid; the whole is diluted with water and placed in the cold, when a precipitate of the bi-acid salt is again formed; and this process is repeated until a liquid is obtained which no longer yields a precipitate. It still contains oleic acid, to obtain which it is concentrated and decomposed with an excess of tartaric acid.

The collected precipitates, after drying, are boiled three times in succession with 8 parts of alcohol of sp. gr. 0·82, and filtered boiling. The first filtrate solidifies completely on cooling, the last does not form a deposit. The deposits are collected, washed with strong alcohol, pressed and crystallised from alcohol, till the acid which is separated from them exhibits the melting point of stearic acid. From the pure bi-acid salt the stearic acid (or margaric acid when human fat is employed) is obtained by heating with aqueous hydrochloric acid (Chevreul).

On saponifying a fat which yields both stearic and margaric acids, *e. g.* hog's lard, beef- or mutton-suet, there is obtained by this process a mixture of bi-margarate and bi-stearate of potash, the latter of which crystallises first from an alcoholic solution (Chevreul). The separation of the bi-acid salts is more easily effected by freezing

the dilute liquid and allowing it to thaw at a temperature of 50°. Hydrochloric acid, to the amount of one-thirtieth of the fatty acids, may also be added to the solution, especially when an excess of potash is present in the soap (Gusserow).

3. *Preparation of Margaric and Stearic acids.* The fatty acids obtained by decomposition of the soaps are digested with 6 volumes of alcohol of sp. gr. 0·835 at 15°; the product is filtered after two or three days, and the undissolved portion is treated afresh with 4 volumes of alcohol. — If the portion still remaining undissolved be then dissolved in 10 or 12 pts. of boiling alcohol, and cooled to − 10 or − 12·5°, it throws down, in the first crystallisation, stearic acid, in the second and third, mixtures of various acids, and in the fourth, margaric acid (Gusserow, *Br. Arch.* 27, 154). See the similar process of Joss (*Schw.* 69, 329).

Properties of Palmitic acid. Small, white scales, which melt at 62° and solidify in the form of a crystalline scaly mass, generally somewhat flowery on the surface, and having a lamellar crystalline fracture (Heintz). Palmitic acid melts at 63·5° (Maskelyne), 62° (Varrentrapp, Brodie), 60 to 61° (Sthamer), 61 to 62° (v. Borck), at 61° and solidifies at 59° (Duffy); melts at 60° and solidifies at 58° (Schwarz); Chevreul's margaric acid also shows this melting-point; melts at 58·5° (Rochleder) 54·5 to 55° (Smith), solidifies at 55° (Dumas & Stas). The acid of Dumas and Stas forms delicate shining laminæ, and solidifies to fine radiated needles; that of Smith forms radiate groups of needles and solidifies to a wax. Sthamer's acid solidifies in a similar manner. Schwarz's acid forms broad satiny laminæ, and solidifies to a highly crystalline mass. Chevreul's margaric acid solidifies in a confused mass of needles.

Palmitic acid is inodorous, tasteless, and very friable. It is lighter than water. Reddens litmus. — When heated in a dish, it boils and evaporates without residue (Dumas & Stass). On distillation it passes over almost entirely unchanged, and only a little oil is obtained thereby (Frémy); there remains at last a slightly coloured residue, having a melting point of 72°, probably palmitone (Maskelyne); the solidifying point of the distillate is lowered from 58° to 57°, the percentage of carbon somewhat increased (Schwarz), but after recrystallisation, the acid remains unaltered (Frémy). According to Frémy, the acid, after being heated to 300°, crystallises from alcohol in nodules; according to v. Borck and Maskelyne, it is not in any way altered thereby. See also palmitonic acid (p. 366).

			Chevreul.	Dumas & Stas.	Frémy.
32 C	....	192	.... 75·0	.... 75·2 .... 74·02	...... 74·27
32 H	....	32	...... 12·5	.... 12·0 .... 12·55	.... 12·55
4 O	....	32	.... 12·5	.... 12·8 .... 13·43	...... 13·18
C³²H³²O⁴	....	256	.... 100·0	.... 100·0 .... 100·00	.... 100·00

	Varrentrapp.		Stenhouse.	Smith.	Sthamer.
	a.	*b.*			
C	74·37	.... 74·45	...... 74·63	.... 74·53	...... 74·24
H	12·23	.... 12·28	...... 12·48	.... 12·51	... . 12·46
O	13·40	.... 13·27	...... 12·89	...... 12·96	...... 13·30
	100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00

	Rochleder	Schwarz.	Brodie.	Heintz.		Maskelyne.
C ...	74·77	.. ... 74·90	.... 74·98	.... 74·69 to	75·00	.... 74·88
H...	12·30	... .. 12·49	.... 12·48	.... 12·48 „	12·71	.... 12·44
O ...	12·93	.... 12·61	.... 12·54	.... 12·83 „	12·29	.... 12·68
	100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00

The analyses are given in mean numbers. — Frémy regarded palmitic acid as bibasic. Varrentrapp's formula contains 1 at. hydrogen less than the above. — Chevreul gave for margaric acid the formula $C^{35}H^{33}O^4$, and for stearic acid $C^{35}H^{35}O^{3\cdot5}$. Berzelius regarded the formula RO^3 for margaric acid and R^2O^5 for stearic acid (in which $R = C^{33}H^{33\cdot5}$) as more probable. The researches of Varrentrapp and Redtenbacher seemed to show that stearic acid is bibasic and $= C^{68}H^{68}O^7$; margaric acid $= C^{34}H^{34}O^4$. The correctness of this view was doubted only by Laurent & Gerhardt (*Compt. rend.* 28, 400), who considered the two acids to be isomeric, and was otherwise generally accepted, till margaric acid was shown by Heintz to be a mixture. — For Pohl's views on the formulæ of the fatty acids see *Wien. Akad. Ber.* 10, 485.

Decompositions. 1. By *heat*, see above; also the statement of Schwarz, under *Palmitonic acid* (p. 366). — 2. Palmitic acid is *combustible*. — 2a. It absorbs *ozone* but slowly, even in presence of an excess of alkali, much of the acid remaining unaltered after exposure to the gas for weeks: carbonic, but no other acid is formed thereby (Gorup-Besanez, *Ann. Pharm.* 125, 215). — 3. It is very slowly attacked by hot *nitric acid* (Maskelyne). Margaric acid, when pure, yields with nitric acid only succinic acid, and neither sebacic nor pimelic acid (Sacc, *Ann. Pharm.* 53, 229). It is not altered by *nitrous acid* (H. Meyer, *Ann. Pharm.* 35, 187).

4. When margaric acid is heated to 120° with *peroxide of lead*, a copious evolution of water-vapour takes place (with which a little carbonic acid is mixed, only if too great a heat be applied) and the brown mass is decolorised, and becomes thick and tenacious. It still contains undecomposed margaric acid; after cooling therefore, it is powdered and boiled with alcohol; the undissolved lead-salt is decomposed with hydrochloric acid; and the acid separated thereby is heated afresh with peroxide of lead. The newly formed lead-salt again decomposed with hydrochloric acid, yields an acid which, when freed as much as possible from margaric acid by dissolving it in alcohol, and removing the crystals first formed in the solution, melts at 47°, and contains 72·05 p. c. C., 12·44 H.; in the lead-salt 53·6 p. c. C., 8·7 H., 28·7 PbO.; and in the silver-salt 29·02 p. c. AgO.; it is therefore probably $C^{34}H^{34}O^5$ (Bromeis, *Ann. Pharm.* 42, 70).

5. When margaric acid is melted together with two or three parts of anhydrous phosphoric acid, the mixture becomes very hot: after the reaction is over, boiling water separates jelly-like lumps of a substance which floats on the surface without melting, but after washing and drying, forms a friable mass melting below 100°. It still contains margaric acid, which is extracted by boiling alcohol or caustic potash, whereupon the undissolved portion settles to the bottom in the form of an oil, but on cooling again floats on the surface as a brittle, brown, scarcely crystalline mass. This last melts at 60° to 65°, dissolves easily in ether, and contains, on an average, 80·31 p. c. C., 12·70 H., and 6·98 O. ($C^{32}H^{30}O^3 = 80·67$ C., 12·60 H. [Kr.]). It is attacked by nitric acid when heated therewith, and yields, when the acid is highly concentrated, a soft, waxy substance; with a moderately dilute acid, a brittle product, the latter containing, on an average, 77·25 p. c. C., 12·22 H., and 10·53 O. (Erdmann, *J. pr. Chem.* 25, 500).

6. Palmitic acid is not perceptibly acted upon by *chlorine* in the cold, but at a temperature of 100° it evolves hydrochloric acid, and does not afterwards solidify on cooling. By this reaction, products containing $\frac{1}{2}$, 1, and $1\frac{1}{2}$ at. of chlorine are obtained, and at length, when 4 at. have been substituted, the action becomes slower or ceases altogether, but may be prolonged with the aid of heat and sunlight, and in that case solid resinous acids are formed (Frémy). An acid prepared in this manner contained, after treatment for 14 days, 60 p. c. chlorine; another acid, prepared out of sunshine, contained 49·4 p. c. C., 7·2 H., and 34·2 Cl.; the latter is sticky, and forms uncrystallisable salts; it is produced also by passing chlorine into palmitic acid melted under water (Frémy): $C^{32}H^{28}Cl^4O^4 = 48·72$ p. c. C., 7·11 H., 36·0 Cl.

7. On distilling palmitic acid with quick *lime* or hydrate of lime, palmitone and carbonate of lime are obtained (Piria, Maskelyne):

$$2C^{32}H^{32}O^4 = C^{62}H^{62}O^2 + 2CO^2 + 2HO.$$
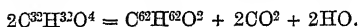
Margaric acid, distilled with ¼th its weight of quick lime, yields first a little water, then a soft mass containing margarone, and at length, towards the end of the distillation, a coloured empyreumatic product; carbonate of lime and charcoal remain behind (Bussy). When a larger proportion of lime is employed, a liquid distillate is obtained, from which margarone cannot be separated; probably a hydrocarbon (Varrentrapp). — Palmitic acid is not altered by heating to 275° with *potash-lime* in a closed vessel; if air be admitted, a little butyric acid is formed, with separation of charcoal, but no fixed fatty acid; the greater part of the palmitic acid is recovered unchanged from the residue (Heintz). When palmitic acid is heated to low redness with excess of potash-lime, gaseous and liquid hydrocarbons containing equal numbers of carbon- and hydrogen-atoms are formed (Cahours, *Compt. rend.* 31, 142). Margaric acid, distilled with excess of potash, yields, besides gaseous products, a light liquid of varying boiling point: Mitscherlich's *Saponin* (Mitscherlich, *Pogg.* 31, 634). A mixture of palmitate and formate of lime yields, on distillation, products similar to those obtained from a mixture of myristate and formate (p. 212) (Limpricht).

8. With *wood-spirit, alcohol, amylic alcohol,* and *mannite,* palmitic acid forms the corresponding ethers, with elimination of water.

From palmitic acid and *glycerin,* neutral compounds belonging to the class of *glycerides* are obtained, with elimination of water; in their modes of formation and decomposition, these compounds exhibit the relations which obtain generally in the compounds of glycerin with monobasic acids.

The *formation* of glycerides takes place by direct contact of their components, slowly at ordinary temperatures, more quickly at elevated temperatures in sealed tubes: in the former case, only small quantities are for the most part produced; and even in the latter case, the union is never complete, since a portion of the fatty acids, and also a portion of the glycerin, when employed in the free state, always remains uncombined. — Some of the glycerides may also be obtained by the action of glycerin on the compound ethers.

On heating a mixture of glycerin with fatty acids, after addition of phosphoric, sulphuric, hydrochloric, or tartaric acid, glycerides of the fatty acids are likewise obtained; but their formation is accompanied by that of other glycerides containing two acids. Thus on heating together stearic acid, glycerin, and hydrochloric acid, single atoms of these substances combine to form stearochlorhydrin, 4 at. water being eliminated:

$$C^{36}H^{36}O^4 + C^6H^8O^6 + HCl = C^{42}H^{41}ClO^6 + 4HO.$$

When benzochlorhydrin ($C^{20}H^{11}ClO^6$, the compound resulting from the combination of single atoms of glycerin, hydrochloric acid, and benzoic acid, with elimination of 4 at. water) is heated to 240° with margaric acid for four hours, *benzomargaro-chlorhydrin* (probably $C^6H^8O^6 + C^{14}H^6O^4$ + HCl + $C^{34}H^{34}O^4$—6HO) appears to be formed (Berthelot, *Chim. organ.* 2, 146).

a. *Monopalmitin.* From 1 at. palmitic acid and 1 at. glycerin, with elimination of 2 at. water:

$$C^{32}H^{32}O^4 + C^6H^8O^6 = C^{32}H^{31}O^3,C^6H^7O^5 + 2HO.$$
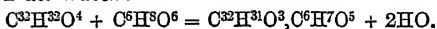
It is produced in small quantity when a mixture of palmitic acid and glycerin is kept for a long time at ordinary temperatures, and in larger quantity when palmitic acid is heated to 200° with an excess of glycerin for 24 hours.

b. *Bipalmitin.* From 2 at. palmitic acid and 1 at. glycerin, with elimination of 2 at. water:

$$2C^{32}H^{32}O^4 + C^6H^8O^6 = 2C^{32}H^{31}O^3,C^6H^8O^6 + 2HO.$$
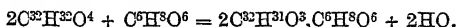
In the formation of other biglycerides, 4 at. water are eliminated. — Bipalmitin is obtained by heating glycerin with an excess of palmitic acid to 100° for 114 hours. The corresponding compounds of stearic acid (also of arachidic and oleic acid) are produced by heating monostearin with excess of stearic acid for 3 hours to 260°, or by heating tristearin to 200° for 22 hours with an excess of glycerin.

c. *Terpalmitin.* From 3 at. palmitic acid and 1 at. glycerin, with elimination of 6 at. water:

$$3C^{32}H^{32}O^4 + C^6H^8O^6 = 3C^{32}H^{31}O^3,C^6H^5O^3 + 6HO.$$
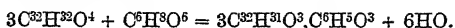
It is obtained by heating monopalmitin to 250° for eight hours, with a very great excess of palmitic acid. In the preparation of the other terglycerides, the compounds corresponding to bipalmitin answer better.

The glycerides resemble the natural fats. The terglycerides are identical with the natural fats, so that palmitin must be contained in those fats which yield glycerin and palmitic acid when saponified. Hence the statements formerly made (vii, 235), require correction.

For the *separation of the glycerides* from the mixtures obtained by heating the fatty acids with glycerin, Berthelot employs the following method : The tube is cooled and opened, and the solid layer containing the glyceride and the uncombined fatty acid which floats on the excess of glycerin employed, is melted, and mixed, first with a little ether, afterwards with hydrate of lime. The mixture is heated to 100° for a quarter of an hour, whereupon the fatty acid combines with the lime, and the glyceride is then extracted by ether, which leaves it behind on evaporation.

The *decompositions of the glycerides* agree with those of the natural fats given on pp. 231 and 240, vol. vii. The following decompositions, which are common to both the natural and artificial glycerides, must be mentioned in addition :

a. Fuming hydrochloric acid, at 100°, resolves them into glycerin and the respective acids. In some cases acetic acid effects the same decomposition.

b. Water decomposes some of the glycerides at 100°, and the greater part, especially those of the fatty acids, at 220°, in sealed tubes, in the same manner.

c. Alcoholic hydrochloric acid decomposes them at 100°, producing an ether and glycerin. — Alcoholic acetic acid partially decomposes the glycerides of palmitic acid at 100°, but not those of stearic and oleic acids.

d. Ammonia separates the glycerin by uniting with the acid to form an amide.

e. The pancreatic juice effects the decomposition of glycerides into

fatty acids and glycerin, even at ordinary temperatures (Bernard, *Compt. rend.* 28, 249, and 283). See *Handbuch* viii. *Zoochem.* 83.

So according to Berthelot (*N. Ann. Chim. Phys.* 41, 216). See also ix. 490.

Combinations. Palmitic acid is insoluble in *water.* — It dissolves in *oil of vitriol,* and is precipitated unaltered by water (Maskelyne). For the behaviour of margaric acid see *Olive-oil.*

Palmitates. Palmitic acid forms salts with bases; those of the alkalis are soluble in water and alcohol. They are all obtained in the same way as the myristates (p. 212) — The margarates (and palmitates) of the alkalis are decomposed by a large quantity of water, into a bi-acid salt which is precipitated, and a solution in which a small quantity of acid remains, together with half the alkali. — Margaric acid expels carbonic acid from carbonates of the alkalis when heated therewith (Chevreul). When warmed with aqueous neutral phosphate of soda, it forms an emulsion in which the fat-globules disappear on boiling : the solution prepared at the boiling heat contains margarate of soda ; that prepared at 30° to 40° contains very little (Marcet, *Kopp's Jahresb.* 1858, 306).

Palmitate of Ammonia. — Crystallised margaric acid absorbs gaseous ammonia more slowly than stearic acid, and forms with it a compound which behaves like the corresponding stearate. It dissolves in hot water, at least in ammoniacal water, and on cooling, the whole of the acid, together with a portion of the ammonia, is thrown down as acid salt. The acid dissolves also in dilute aqueous ammonia to a clear liquid, which gives off ammonia in the air ; with concentrated ammonia it forms a translucent jelly (Chevreul).

A palmitate of ammonia prepared by Frémy appears to be *bi-acid.* It is deposited even from strongly ammoniacal solutions, and is insoluble in cold water.

				Frémy.
64 C	384	72·59	71·94
N	14	2·65	3·00
67 H	67	12·66	12·70
8 O	64	12·10	12·36
$C^{32}H^{31}(NH^4)O^4,C^{32}H^{32}O^4$	529	100·00	100·00

Palmitate of Potash. — a. *Mono-acid..* Palmitic acid is fused with carbonate of potash, and the resulting mass is exhausted with boiling alcohol, from which the salt crystallises on cooling. — White, pearly scales, fusible without decomposition or loss of weight. — One part of dry margarate of potash forms, with 10 pts. of water at 12°, a semi-transparent gum ; at 70°, a transparent liquid which, on cooling to 60°, exhibits pearly streaks ; at 36°, the solution becomes thicker and less transparent, but is not gummy even at 15° ; when 90 pts. water are added to the liquid, it turns thick and milky in 24 hours, and runs slowly through the filter, upon which a deposit of the pearly bi-acid salt is left (Chevreul). — Palmitate of potash is soluble in hot alcohol, insoluble in ether (Dumas & Stass). Margarate of potash dissolves in 82·3 pts. alcohol, of sp. gr. 0·834 at 10° ; the solution in 10 pts. boiling alcohol becomes turbid at 43°, throws down flakes and a gelatinous sediment, and congeals at 38° to a solid opaque jelly (Chevruel).

				Chevreul.	Dumas & Stas.
32 C	192·0	65·27			64·09
31 H	31·0	10 53			10·90
3 O	24·0	8 16			9·32
KO	47·2	16·04	15·00		15·69
$C^{32}H^{31}KO^4$	294·2	100·00			100·00

b. *Bi-acid.* — When a solution of 1 pt. margarate of potash in 20 pts. boiling water is mixed with 1,000 pts. cold water, and the precipitate

thereby produced is collected on a filter and dissolved, after drying, in boiling alcohol, small pearly leaves of the bi-acid salt are obtained on cooling. From these, cold water takes up only a trace of potash, boiling water a little more potash and a trace of acid. The salt dissolves in 323 pts. alcohol of sp. gr. 0·834 at 20°, and in 3·2 pts. at 67°. Water precipitates, from the alcoholic solution, a salt containing less potash (Chevreul). — Schwarz obtained a bipalmitate of potash by saponifying palm-oil and crystallising the soap from alcohol. It was deposited in the form of nodules, and melted at 100° to a semi-transparent mass.

						Chevreul.		Schwarz.
$C^{64}H^{63}O^7$		503	....	91·42	....			
KO		47·2	....	8·58	....	8·07	....	8·30
$C^{32}H^{31}KO^4,C^{32}H^{32}O^4$		550·2	....	100·00	....			....

Palmitate of Soda. — a. *Mono-acid.* — Prepared in the same way as myristate of soda (p. 212). — Broad, pearly laminæ (Dumas & Stas). The salt separates from an alcoholic solution in the form of a jelly, which, on standing with a sufficient quantity of alcohol, changes to colourless laminæ (Heintz). — More easily decomposed by water than the potash-salt (Dumas & Stas). A solution of 1 pt. margarate of soda in 600 parts water becomes turbid in 14 days, and afterwards dissolves only a trace of the acid. One part of the salt in 10 parts water, at 80°, forms a clear solution which shows a slight turbidity on cooling to 70°; at 57° silky stars make their appearance, and at 53° the liquid is converted into a solid opaque jelly, from which the liquid portion may be expressed. 1 pt. forms a clear solution with 50 pts. water below 100°. The solution in 100 parts of hot water deposits fine needles of a slightly acid salt on cooling, one-fourth of the soda remaining in solution; from this acid-salt, boiling water takes up the mono-acid salt, whilst bi-acid salt is left behind (Chevreul). Margarate of soda dissolves in 262 parts of alcohol of sp. gr. 0·821 at 10°, and in 20 parts at 79°; the latter solution throws down a flocculent deposit at 72°, and becomes turbid; at 62° it begins to be gelatinous, and at 58° solidifies completely to a jelly from which alcohol does not separate, and in which no crystals are formed. A solution of 1 part of the salt in 30 parts of hot alcohol forms, when cold, a pellucid bluish jelly without crystals (Chevreul).

							Heintz.
32 C		192	....	69·06	....	68·67	
31 H		31	....	11·15	....	11·15	
3 O		24	....	8·64	....	9·13	
NaO		31	....	11·15	....	11·05	
$C^{32}H^{31}NaO^4$		278	....	100·00	....	100·00	

Contains 11·18 p. c. soda (Maskelyne). Margarate of soda contains 11·06 p. c. soda (Chevreul).

b. *Bi-acid.* — Mono-margarate of soda is dissolved in 1500 parts of hot water, and the solution is cooled and filtered; the precipitate, after drying, is dissolved in alcohol; the solution is again cooled; and the bi-acid salt thus obtained is pressed and dried. It is white and tasteless, more fusible than a, insoluble in water, very easily soluble in hot alcohol. The solution reddens litmus, the blue colour being restored by water (Chevreul).

						Chevreul.
$C^{64}H^{63}O^7$		503	....	94·19	....	
NaO		31	....	5·81	....	5·62
$C^{32}H^{31}NaO^4,6^{32}H^{32}O^4$		534	....	100·00	....	

Palmitate of Baryta.—White, pearly, crystalline powder. Decom-

poses before melting (Heintz).   Does not soften at 100°.   (Varrentrapp).

					Heintz.
32 C	....	192·0	....	59·37	.... 59·04
31 H	....	31·0	....	9·59	.... 9·74
3 O	....	24·0	....	7·42	.... 7·53
BaO	....	76·5	....	23·62	.... 23·69
C³²H³¹BaO⁴	....	323·5	....	100·00	.... 100·00

Contains 23·01 (Varrentrapp), 22·91 (Stenhouse), on the average 23·61 p. c. baryta (Maskelyne).   Margarate of baryta contains 22·31 p. c. baryta (Chevreul).

Margarate of Strontia. — Margaric acid is digested for two hours in a closed vessel with an excess of strontia-water which is filtered into it at the boiling heat. The precipitated salt is freed from excess of strontia by pouring off the liquid and boiling with water, and from free acid by boiling alcohol (Chevreul).

					Chevreul.
C³²H³¹O³	....	247	....	82·61	....
SrO	....	52	....	17·39	.... 16·34
C³²H³¹SrO⁴	....	299	....	100·00	

Margarate of Lime. — Precipitated from chloride of calcium by boiling monomargarate of potash, and washed with boiling water (Chevreul).

					Chevreul.
C³²H³¹O³	....	247	....	89·82	....
CaO	....	28	....	10·18	.... 9·97
C³²H³¹CaO⁴	....	275	....	100·00	

Palmitate of Magnesia. — Snow-white, very loose crystalline precipitate, which dissolves in boiling alcohol and crystallises almost completely, on cooling, in microscopic rectangular laminæ.   It melts at about 120° without decomposition (Heintz).

					Heintz.
32 C	....	192	....	71·27	.... 71·91
31 H	....	31	....	11·61	.... 11·61
3 O	....	24	....	9·51	.... 8·99
MgO	....	20	....	7·61	.... 7·49
C³²H³¹MgO⁴	....	267	....	100·00	.... 100·00

Contains, on the average, 8·02 p. c. magnesia (Maskelyne).

The palmitates of *zinc*, *tin* (stannous), and *iron* (ferrous), are white precipitates; the *ferric salt* is dark-yellow, the protosalt of *cobalt* rose-red (Dumas & Stass).

Palmitate of Lead.   Palmitic acid loses 3·74 p. c. when heated with oxide of lead (v. Borck).   Margaric acid loses 3·4 p. c. water thereby (Chevreul). (1 at. = 3·51 p. c.)

a. *Basic ?* — When margaric acid is boiled with terbasic acetate of lead, access of air being prevented, a compound with 45·59 p. c. oxide of lead is obtained (Chevreul). (C³²H³¹PbO⁴,PbO = 47·56 p. c. PbO).   By heating mono-margarate of lead for several days with basic acetate of lead, Varrentrapp obtained a salt containing acetic acid, with 29·44 p. c. C., 4·67 H., and 59·94 PbO.

b. *Mono-acid.*—Snow-white, microscopic scales, which melt at 108°

(Maskelyne), 110° to 112° (Heintz), and solidify to a white, opaque, amorphous mass (Heintz). By fusing an excess of the acid with oxide of lead and separating the uncombined acid by ether, it is obtained as a friable, white wax, which melts at 112°, and is nearly insoluble in alcohol and ether (v. Borck).

				Frémy.	Heintz.	Maskelyne.
32 C	192	53·54	51·87	53·57	53·74
31 H	31	8·65	8·29	8·62	8·86
4 O	32	8·92	10·40	8·83	7·91
Pb	104	28·89	29·44	28·98	29·49
C^{32}H^{31}PbO^4	359	100·00	100·00	100·00	100·00

Chevreul found 29·45 p. c. oxide of lead.

Palmitate of Copper.—Pale green-blue, very loose powder, consisting of extremely small microscopic laminæ. It melts, when heated, to a green liquid which is rapidly decomposed (Heintz).

			Heintz.	Maskelyne.
32 C	192	66·98	66·65	
31 H	31	10·82	10·78	
3 O	24	8·37	8·54	
CuO	40	13·83	14·03	14·07
C^{32}H^{31}CuO^4	287	100·00	100·00	

Mercurous Palmitate is a white precipitate (Dumas & Stas).—Margarate of potash precipitates from mercurous nitrate, flocks which soon cohere to a mass of the consistence of ointment, and harden on drying. They contain 44·15 p. c. Hg^{2}O, and are insoluble in water, slightly soluble in alcohol and ether (Harff, *N. Br. Arch.* 5, 308).

Mercuric Margarate. — By heating margaric acid with mercuric oxide, or by precipitating mercuric nitrate with margarate of potash, white flocks are obtained, which are quickly transformed into a greasy mass, drying up very slowly in the air. It contains 27·44 p. c. HgO. Insoluble in water and cold alcohol; slightly soluble in hot alcohol, and much more freely in ether (Harff).

Palmitate of Silver.—Thrown down from cold solutions as a light, somewhat gelatinous, and from hot solutions as a granular precipitate, which in the moist state blackens on exposure to light, but not when dry (Varrentrapp). It appears amorphous even when highly magnified (Heintz).—Dissolves slightly in water (Varrentrapp). Separates from a solution in warm ammonia-water in indistinct scales (v. Borck).

			Frémy.	Varrentrapp.	Stenhouse.
32 C	192	52·89	52·78	52·80	52·82
31 H	31	8·54	8·61	8·43	8·60
4 O	32	8·85	9·75	9·49	9·29
Ag	108	29·72	28·86	29·28	29·29
C^{32}H^{31}AgO^4	363	100·00	100·00	100·00	100·00

	Smith.	v. Borck.	Sthamer.	Brodie.	Heintz.	Maskelyne.
C	52·57	52·51	52·21	53·27	52·71	52·99
H	8·47	8·58	8·53	8·76	8·53	8·44
O	9·41	9·58	9·64	8·53	9·01	8·83
Ag	29·55	29·33	29·62	29·44	29·75	29·74
	100·00	100·00	100·00	100·00	100·00	100·00

The silver-salt analysed by v. Borck was crystallised from ammonia.

Palmitic acid is soluble in *alcohol;* in all proportions in alcohol of sp. gr. 0·82 at 40° (Smith).—It dissolves readily in *ether.*

From a solution of palmitic acid and glycocol (ix. 247) in warm alcohol, there separates on cooling an oily layer which afterwards solidifies; the liquid beneath throws down white silky laminæ, containing, when dried over oil of vitriol, 51·30 p. c. C., and 9·45 H. (Horsford, *Ann. Pharm.* 60, 29).

Palmitic acid may be melted together with *lauric* and *myristic acids.* In certain proportions the mixtures are not separable by crystallisation from alcohol or ether: they exhibit the following characters on melting and solidifying (Heintz):—

A mixture of—		Melts at	Mode of Solidifying.
Palmitic acid.	Lauric acid.		
10	90	41·5°	Uncrystallised.
20	80	37·1°	Finely crystallised, indistinct.
30	70	38·3°	Small-leaved, crystalline.
.40	60	40·1°	Splendid large laminæ.
50	50	47·0°	Opaque, scarcely crystalline.
60	40	51·2°	Granular, distinctly scaly.
70	30	54·5°	More distinctly scaly.
80	20	57·4°	Still more distinctly scaly.
90	10	59·8°	Crystalline scales.

A mixture of—		Melts at	Solidifies at	Mode of Solidifying.
Lauric acid.	Myristic acid.			
95	5	61·1°	58°	Crystalline scales.
90	10	60·1°	55·7°	„ „
80	20	58·0°	53·5°	Scales, with slight admixture of needles.
70	30	54·9°	51·3°	Very delicate needles.
60	40	51·5°	49·5°	Uneven, uncrystallised.
50	50	47·8°	45·3°	Large laminæ.
40	60	47·0°	43·7°	Indistinctly lamellar.
35	65	46·5°	..	Uncrystallised, opaque.
32·5	67·5	46·2°	44·0°	„ „
30	70	46·2°	43·7°	„ „
20	80	49·5°	41·3°	Uncrystallised.
10	90	51·8°	45·3°	Long needles.

Palmitic, Myristic and Lauric acids.—A mixture of 30 p. c. myristic and 70 p. c. lauric acid melts at 35·1°; when to 20 parts of this mixture from 1 to 10 parts palmitic acid are added, the melting points of

the resulting mixtures are altered, according to Heintz, as follows :—
On addition of,

Palmitic acid.		The melting point is—	Palmitic acid.		The melting point is—
1 part	....	33·9°	6 parts	....	34·6°
2 ,,	....	33·1°	7 ,,	....	35·3°
3 ,,	....	32·2°	8 ,,	....	36°
4 ,,	....	32·7°	9 ,,	....	37·3°
5 ,,	....	33·7°	10 ,,	....	38·8°

The mixtures containing 9 and 10 parts palmitic acid solidify in delicate needles, the others in the non-crystalline form (Heintz).

Interpolation.

The following have been described as *peculiar fatty acids.* Their identity with known acids, or the fact of their being mixed acids, is either already established, or has at least been shown to be probable.

Anthropic acid. An acid obtained from human fat, formerly described by Heintz as a peculiar acid, but afterwards found to be a mixture of palmitic and stearic acids.

Bassic acid. The stearic acid obtained by Hardwicke from oil of Bassia. The remarks of Heintz on Bassic acid (*Pogg.* 92, 601) refer to another acid of 55° melting-point, obtained from the same oil. See under *Bassia-oil.*

Benic acid of Walter. *Behensäure.* Occurs in very small quantity in oil of ben. It crystallises from alcohol in light nodules which melt at 52° to 53°. Contains 74·3 p. c. C., 12·5 H., and 13·2 O.; according to Walter, $C^{30}H^{30}O^{4}$. It dissolves more readily than margaric acid in alcohol. The ethyl-compound is a crystalline mass, which melts in the hand, and is very easily soluble in alcohol; it contains 75·8 p. c. C., 12·7 H., and 11·5 O. (Walter, *Compt. rend.* 22, 1143). See Laurent (*N. Ann. Chim. Phys.* 19, 374). Heintz regards this acid as a mixture of 75 parts palmitic and 25 parts myristic acid. Concerning the benic acid of Mulder, see under compounds with 44 at. C.

Butyroleic acid. The oleic acid of common butter, which was supposed by Bromeis (*Ann. Pharm.* 42, 46) to differ from ordinary oleic acid; this supposition was refuted by Heintz.

Butyrolimnodic acid. See *Bog-butter.*

Cetic acid. An acid obtained from spermaceti ($C^{30}H^{30}O^{4}$); thus named by Heintz, who afterwards found it to be a mixture.

Cocinic acid. (See xv, 44).

Coculostearic acid. Berzelius thus designated the stearic acid obtained from cocculus-grains.

Isocetic acid. In the oil of *Jatropha Curcas.* It is separated by expressing the fatty acids. Crystallises from alcohol in shining laminæ. Melts at 55°; solidifies at 53·5°. Its composition is $C^{30}H^{30}O^{4}$.
— The silver-salt melts when heated, and dissolves freely in boiling

alcohol. — The ethyl-compound C³⁰H²⁹O³,C⁴H⁵O solidifies at 21° to a translucent crystalline mass. — *Isocetamide*, C³⁰NH³¹O², obtained by digesting Jatropha-oil for two months (a shorter time when heated) with alcoholic ammonia, is white and pearly, and melts at 96·5° (*Par. Soc. Bull.* 1, 74; Bromeis, *Compt. rend.* 39, 923). Probably a mixture of 70 parts palmitic and 30 parts myristic acid (Kr.).

Madic acid. The acid, melting at 54° to 55°, obtained by Luck from oil of madia. According to Heintz, it is a mixture of stearic and palmitic, and perhaps a third acid.

Olidic acid. The palmitic acid resulting from the decomposition of oleic acid by caustic potash.

Palmic acid. Boudet termed the product of the action of nitrous acid on castor-oil, palmin; the acid obtained from the fat he called palmic acid. (See *Ricinelaı̈lic acid.*)

Palmitonic acid. Schwarz (*Ann. Pharm.* 60, 58) found, on attempting to purify commercial palmitic acid (prepared from palm-oil freed from oleic acid by pressing, and from colouring matters by melting in contact with the air) by saponifying and recrystallising from alcohol, that the melting-point remained constant at 52·5° to 53°, and the solidifying point at 51°, and that they were not altered by saponifying the acid and decomposing the soap. This acid, distinguished by Schwarz as palmitonic acid, is, according to Heintz, a mixture of palmitic and myristic acids. It crystallises in dull, white, granular masses, and solidifies, after melting, to a semi-transparent, wax-like substance, having a slightly fibrous fracture and a wavy surface. By distillation it is obtained with lower melting-point and higher percentage of carbon (76·43 p. c. C., 13·02 H.), but after crystallising from alcohol it remains unaltered. With nitric acid it forms suberic acid; the unchanged portion of the acid retains its melting-point unaltered. The acid contains 74·70 p. c. C., 12·41 H. (mean); the baryta-salt 60·35 p. c. C., 9·82 H., 21·55 BaO, in another preparation 26·02 BaO; the silver-salt 55·65 p. c. C., 9·50 H., 26·36 Ag.; the ethyl-compound, a distinctly crystalline solid at 25°, contains 75·84 p. c. C., 12·57 H., after distillation 76·2 p. c. C., 12·74 H. According to Schwarz, this acid is also produced by the prolonged heating of palmitic acid to 250° or 300°, but Maskelyne did not find this to be the case. Schwarz's formula is C³¹H³¹O⁴.

Solanoleic and *Solanostearic acids.* See *Potato-fat*

Stearophanic acid. The solid fatty acid prepared from cocculus-grains, to which this name and the formula C³⁵H³⁵O⁴ were ascribed by Francis; its identity with Hardwicke's bassic acid was recognised by Crowder. Heintz at first designated the acid obtained from human fat and spermaceti, as stearophanic acid, but afterwards perceived the identity of this and of bassic acid with stearic acid.

Stillistearic acid. Chinatalgsäure. The fatty acid, melting at 62°, separated from Chinese wax, to which v. Borck gave the formula C³⁰H³⁰O⁴. Doubtless identical with palmitic acid (Maskelyne, Heintz). See the analyses of palmitic acid·

Sulphide of Cetyl.

$$C^{32}H^{33}S = C^{32}H^{32},HS.$$
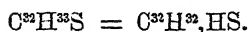
FRIDAU. *Ann. Pharm.* 83, 16.

Cetylsulfür.

Formed by boiling chloride of cetyl for several hours with alcoholic monosulphide of potassium; it separates from the liquid, on cooling, · as an oily layer which afterwards solidifies, and in flocks. It is purified by washing and re-melting with water, and crystallising, first from weak, then from strong boiling alcohol, or from ether-alcohol.

Light, silvery laminæ, which melt at 57·5°, and solidify at 54° to a radiated mass. — It is but slowly altered by boiling with dilute nitric acid. — It is precipitated from an alcoholic solution (from a cold saturated solution only after long standing) by alcoholic neutral acetate of lead, in white flocks which are insoluble in water, alcohol, and ether.

Sulphide of cetyl dissolves very slightly in cold alcohol, more freely in boiling alcohol, and easily in ether.

				Fridau.
32 C	192	79·67		79·36
33 H	33	13·69		13·71
S	16	6·64		
	241	100·00		

Cetyl-mercaptan.

$$C^{32}H^{34}S^2 = C^{32}H^{32},H^2S^2.$$
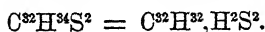
FRIDAU. *Ann. Pharm.* 83, 18.

Cetylsulfhydrat.

When chloride of cetyl is boiled with alcoholic sulphydrate of potassium, a mixture of cetyl-mercaptan and sulphide of cetyl is obtained, which is not separable by crystallisation. The mixture is dissolved in hot alcohol; neutral acetate of lead and then water added to the solution; and the precipitate formed is washed and treated with ether, which takes up the cetyl-mercaptan and leaves behind the lead-compound of sulphide of cetyl. The mercaptan is then purified by recrystallisation.

Cetyl-mercaptan resembles sulphide of cetyl. It melts at 50·5°, and solidifies below 44° to a confused crystalline mass. When boiled with water, it emits a faint peculiar smell.

				Fridau. mean.
32 C	192	74·42		74·50
34 H	34	13·18		12·95
2 S	32	12·40		
$C^{32}H^{34}S^2$	258	100·00		100·00

Cetyl-mercaptan is scarcely acted upon by *mercuric oxide*, even at high temperatures.

It is insoluble in *water*. — A cold alcoholic solution precipitates alcoholic *mercuric chloride* and *nitrate of silver* in white flocks ; it does not precipitate lead-, platinum-, or gold-salts.

Dissolves with difficulty in cold *alcohol*, easily in *ether*.

Iodide of Cetyl.

$$C^{32}H^{33}I = C^{32}H^{32},HI.$$
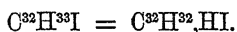
FRIDAU. *Ann. Pharm.* 83, 9.
BECKER. *Ann. Pharm.* 102, 211.

Cetyliodür.

Formation and Preparation. Ethal is heated to a temperature of 100° to 120°, and phosphorus and iodine are alternately added in small portions, until the liquid becomes dark-coloured and iodine-vapours are evolved, care being taken to avoid an excess of these substances, and an elevation of temperature above 160°. The product is then allowed to cool thoroughly, carefully separated from the iodide of phosphorus, washed, so long as the wash-water exhibits an acid reaction, and crystallised from alcohol. The crystals are washed with cold water and alcohol (Fridau). Becker removes ethal by boiling with small quantities of alcohol in which a little iodide of cetyl is dissolved.

Properties. White crystalline laminæ, which melt at 22°, and form a crystalline solid on cooling (Fridau).

							Fridau.
32 C	....	192	....	54·57	....	54·58
33 H	....	33	....	9·38	....	9·48
I	....	127	. ...	36·05	....
C³²H³³I	....	352	....	100·00

Decompositions. 1. *Heated* to about 250°, it decomposes, with evolution of iodine and hydriodic acid, and yields an oily distillate, probably a mixture of different hydrocarbons. — 2. It is not altered by *mercuric oxide* at mean temperatures, but on raising the temperature to about 200°, a violent reaction takes place, mercury, iodide of mercury, and an oil passing over, and crystals having the melting point of ethal remaining in the residue. *Protoxide of lead* acts more slowly, *oxide of silver* not at all ; in the presence of water, however, and at temperatures between 100° and 150°, it forms ethal and iodide of silver (Fridau). — 3. When iodide of cetyl is heated with *cyanide of silver* till the former begins to be decomposed by the heat, a small quantity of iodide of silver is formed ; but ether extracts from the residue nothing but unaltered iodide of cetyl. — When very strongly heated with *cyanide of mercury*, it yields red iodide of mercury, but no cyanide of cetyl (Becker). For the decomposition with *cyanide of potassium*, see *Cyanethal.* — 4. With *ammonia* it forms tercetylamine, no other base being obtained, even when the action is continued for a short time

only. With *aniline*, it forms *cetyl*- and *bicetyl-aniline;* with excess of aniline, only the former. — 5. With *cetylate of sodium*, it forms cetylic ether and iodide of sodium (Fridau); with *ethylate* and *amylate of sodium*, ethyl-cetylic and amyl-cetylic ethers (Becker).

Insoluble in *water*, easily in *alcohol* and in *ether* (Fridau). Sparingly soluble in alcohol (Becker).

Bromide of Cetyl.

$$C^{32}H^{33}Br = C^{32}H^{32},HBr.$$
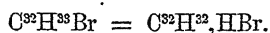
FRIDAU. *Ann. Pharm.* 83, 15.

Bromcetylafer.

Obtained like the iodide, using bromine in place of iodine. The action takes place at 100°. — Formed also by heating cetylene with hydrobromic acid (Berthelot, p. 342).

White, solid mass, melting to an oil at 15°, heavier than water.

					Fridau.		
32 C	....	192	....	62·96	....	62·53
33 H	....	33	....	10·82	....	10·86
Br	....	80	....	26·22	....	
$C^{32}H^{33}Br$	....	305	....	100·00	....	

When *heated*, it turns brown and gives off hydrobromic acid.— *Ammonia* converts it into tercetylamine.

Insoluble in *water;* easily soluble in *alcohol* and in *ether.*

Chloride of Cetyl.

$$C^{32}H^{33}Cl = C^{32}H^{32},HCl.$$
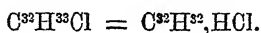
DUMAS & PELIGOT. *Ann. Chim. Phys.* 62, 14.
FRIDAU. *Ann. Pharm.* 83, 9.
BERTHELOT. *N. Ann. Chim. Phys.* 51, 83; *Chim. organ.* 1, 121.
TÜTTSCHEFF. *Zeitschr. Chem. Pharm.* 4, 59; *Kopp's Jahresber.* 1860, 405.
HEINTZ. *Pogg.* 102, 262.

Chlorhydrate de Cetène. Chlorcetylafer.

Formation. 1. From ethal by the action of penta-chloride of phosphorus (p. 346). — 2. From cetylene and hydrochloric acid (p. 342).

Preparation. When equal volumes of ethal and pentachloride of phosphorus are mixed in a retort, the mass melts together, becomes hot, and gives off a large quantity of hydrochloric acid gas. On heating the mixture, chloro-phosphoric acid and chloride of cetyl pass over successively; and the latter may be rectified over a small quantity of pentachloride of phosphorus, washed with water, boiled 5 or 6 times with fresh quantities of water, and finally rectified in a vacuum at

about 120°. When thus prepared, it still however retains traces of hydrochloric acid, from which it may be freed by rectification over a very small quantity of lime (Dumas & Peligot). Heintz mixes 112 gr. pentachloride of phosphorus with 132 gr. ethal; distils; treats the distillate again with a little pentachloride of phosphorus; then washes and dries the product. — See below for the decomposition which takes place during distillation.

Properties. Oily liquid of sp. gr. 0·8412 at 12° (Tüttscheff).

						Dumas & Peligot.
						mean.
32 C	....	192·0	....	73·70	....	72·63
33 H	....	33·0	......	12·66	....	12·26
Cl	....	35·5	......	13·64	....	13·35
$C^{32}H^{33}Cl$	....	260·5	....	100·00	....	98·24

Decompositions. Chloride of cetyl boils at 290° with partial decomposition, blackening, and giving off hydrochloric acid gas, and if the *boiling* be prolonged, is entirely converted into cetylene (Tüttscheff). — It is not altered by *dilute acids*, and scarcely by very concentrated *nitric acid* (Fridau). Oil of vitriol acts upon it gradually, especially if aided by heat, eliminating hydrochloric acid, and forming cetylene-sulphuric acid (Tüttscheff). It is not altered by *potash-ley* (Fridau), and does not absorb *ammonia* (Tüttscheff). — With *protosulphide of potassium* it forms sulphide of cetyl; with *hydrosulphate of potassium*, the same compound, together with cetylic mercaptan (Fridau). Heated with *cyanide of potassium*, it does not yield cyanide of cetyl; neither is it acted upon by *cyanide of mercury*. When heated for 52 hours in a Papin's digester with an equal weight of *cyanide of silver*, it yields a product from which ether extracts a nitrogenous substance, which, when treated with hydrate of potash, gives off ammonia, and forms an acid boiling at 52·7° (Heintz).

Insoluble in *water* and in *alcohol;* soluble in *ether*, and precipitated therefrom by weak alcohol.

Conjugated Compounds of the Primary Nucleus $C^{32}H^{32}$.

Cetylene-sulphuric Acid.

$$C^{32}H^{32}S^2O^6 = C^{32}H^{32}, 2SO^3.$$
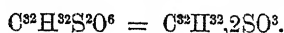
Dumas & Peligot (1836). *Ann. Chim. Phys.* 62, 11.
Fridau. *Ann. Pharm.* 83, 8.
H. Köhler. *Zeitschr. für die gesammten Naturwissenschaften*, 7, 352.
Heintz. *Pogg.* 102, 265.

Sulphocetylic, Sulphocetic or *Cetylsulphuric acid.* Known only as a potash-salt.

Formation. By the action of oil of vitriol upon ethal (p. 346).

Preparation of the Potash-salt. Ethal and oil of vitriol are heated together over the water-bath, with frequent agitation, till the two have united; the product is dissolved in alcohol and saturated with

alcoholic potash, which throws down sulphate of potash, while cetylene-sulphate of potash remains in solution, together with the excess of ethal; and the liquid is filtered, evaporated, and left to crystallise. The crystals are dissolved in absolute alcohol, which leaves behind a small quantity of sulphate of potash; the solution is evaporated, and left to crystallise again; and the salt is triturated and washed with ether, as long as that liquid continues to take up ethal (Dumas & Peligot). The sulphate of potash precipitated on saturating the liquid with alcoholic potash, carries down with it a certain quantity of cetylene-sulphate of potash, which may be dissolved out by boiling alcohol. — The cetylene-sulphate, so long as it retains any ethal, cannot be recrystallised from water, but forms therewith a turbid, flocculent jelly, which cannot be filtered (Köhler). Heintz brings fused ethal in contact with cold oil of vitriol, because by heating the materials in the water-bath, he obtained cetylic ether and palmitic aldehyde, but no cetylene-sulphate.

Properties of the Potash-salt. White, pearly laminæ (Dumas & Peligot), light and loose, soft to the touch, and consisting of slender microscopic needles (Köhler). Infusible; becomes dull when heated above 100° (Köhler); bakes together at 200°, but is little, if at all, decomposed (Heintz). — At a stronger heat, it burns and leaves a grey spongy residue of sulphate of potash (Dumas & Peligot). Sparingly soluble in boiling water, more easily in boiling alcohol, insoluble in ether (Köhler).

					Dumas & Peligot.		Heintz.		
					mean.			*mean.*	
32	C	192	......	53·32	....	52·46	......	53·19	
33	H	33	......	9·16	......	9·15	......	9·14	
	O	8	......	2·22	......	1·64	....	2·73	
2	SO³	80	......	22·21	....	23·76	......	22·00	
	KO	47	......	13·09	....	12·99	....	12·94	

$C^{32}H^{33}KO^2,2SO^3$ .... 360 ...... 100·00 .... 100·00 .... 100·00

The salt analysed probably contained also stethalsulphate of potash.

Cetylene-sulphuric acid cannot be separated from the potash-salt by hydrochloric-acid, because secondary products are formed at the same time (Fridau).

Cetylene-sulphate of potash heated with cyanide of potassium yields cyanide of cetyl (Heintz).

From the aqueous or alcoholic solution of the potash-salt, *baryta* and *silver salts* throw down precipitates which crystallise from alcohol (Fridau). From the dilute alcoholic potash-salt, neutral acetate of lead throws down a white granular precipitate; *cupric acetate* a light blue, fine powder; *mercuric chloride*, a grey, fine-grained precipitate, difficult to collect (Köhler).

Cetyl-xanthic Acid.

$$C^{34}H^{34}S^4O^2 = C^{32}H^{34}O^2,2CS^2.$$
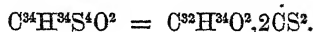
De la Provostaye & Desains. *Compt. rend.* 15, 592; *J. pr. Chem.* 27, 378; in detail, *N. Ann. Chim. Phys.* 6, 494; *J. pr. Chem.* 28, 455.

Cetenxanthonsäure. Carbonylsulfosaures Monocetyl. Known only in combination with bases.

Preparation of the Potash-salt. When finely pulverised hydrate of potash is added to a cold saturated solution of ethal in sulphide of carbon, reaction begins immediately, the potash swelling up, and the mass becoming pasty, solid, and yellowish-red. The liquid after standing for several hours, is diluted with 3 or 4 volumes alcohol of 40°, and heated, but not to boiling; and the pale-yellow solution is poured off from a small quantity of a thick, dark red, strongly alkaline oil and left to cool; it then deposits the potash-salt as a very bulky mass. This is collected, washed with cold alcohol of 36°, re-crystallised from boiling alcohol of 40°, washed with cold alcohol and ether, and dried in a vacuum over oil of vitriol. In the process of precipitation, the greater part of the salt remains in the mother-liquor.

Properties of the Potash-salt. White, soft, crystalline powder, having a faint, fatty odour. Has no alkaline reaction.

When fused it gives off vapours, which at first smell like onions, then of sulphide of carbon, and lastly of ethal, take fire, and leave an alkaline cinder containing sulphide of potassium. Hydrochloric acid moistens it with difficulty, and separates from it a flesh-coloured elastic mass, which soon becomes white and exhibits the characters of ethal. It decolorises an alcoholic solution of iodine (like the xanthates) without evolution of gas, and forms a compound homologous with the compound, $C^6H^5S^4O^2$, of the ethylene series (viii. 455). (Desains: *N. Ann. Chim.* 20, 507). Probably therefore:

$$C^{34}H^{33}KS^4O^2 + I = KI + C^{34}H^{33}S^4O^2.$$
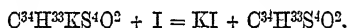
Cetylxanthate of potash is hygroscopic, difficult to moisten, but is decomposed by the continued action of water. It dissolves very easily in warm alcohol and ether, sparingly in the same liquids when cold.

					Provostaye & Desains.
					mean.
34	C	204·0	57·27	57·00
33	H	33·0	9·26	9·29
4	S	64·0	17·98	18·04
	O	8·0	2·24	2·31
	KO	47·2	13·25	13·36
$C^{34}H^{33}KS^4O^2$		356·2	100·00	100·00

The *baryta-salt* is prepared similarly to the potash-salt, with anhydrous baryta, but the action is slower. The resulting gelatinous mass, purified like the potash-salt, contains 20·28 p. c. baryta.

The aqueous solution of the potash-salt precipitates a white jelly from *zinc-salts.* — With *neutral acetate of lead*, it forms a bulky white precipitate which blackens on standing. — From *mercuric chloride*, it throws down a white curdy precipitate, which becomes yellow during washing and decomposes in contact with the filter. — From *nitrate of silver*, it throws down a light yellow precipitate, which soon turns yellow and black, even in the dark.

Chlorohydrate of Cetylene.

$$C^{32}ClH^{33}O^2 = C^{32}H^{32},ClHO^2.$$
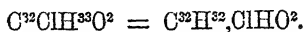
CARIUS. *Ann. Pharm.* 126, 201.

Cetylic chlorhydrin.

Formation. From cetylene (p. 341)and hypochlorous acid.

$$C^{32}H^{32} + ClO,HO = C^{32}H^{33}ClO^2.$$
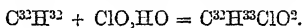
Preparation. A number of stoppered bottles, each holding not more than a litre, are filled with chlorine gas as free as possible from air, and set in a dark place; to each litre of chlorine is added 15 grms. of precipitated mercuric oxide—previously heated to 300°, then left to cool, and suspended in a small quantity of water; and the bottles, after being shaken, are left for a quarter of an hour, by which time the greater part of the mercuric oxide is converted into oxychloride. To the aqueous hypochlorous acid thus obtained—which must be diluted till it contains at most 1 p. c. of acid, left in contact with the mercury-compound, and cooled with ice-cold water—cetylene is added by small portions, and with frequent agitation, till the hypochlorous acid completely disappears. The resulting chloro-hydrate mixes with the mercuric oxide at the bottom of the vessels, and must be dissolved out by ether, separated by evaporation of the ether, freed from admixed chloride of mercury by agitation with sal-ammoniac, then washed and dried. After this treatment, it still retains a small quantity of cetylene, from which it may be freed by prolonged heating to 250° in a stream of carbonic acid.

Properties. Colourless oil, which at 15° becomes very viscid but does not solidify. It boils at about 300° and distils without decomposition. Small quantities of hydrochloric acid gas which escape at the same time, and a little residual charcoal, appear to arise from a product richer in chlorine (perhaps $C^{32}H^{32}Cl^2$), which has not been removed in the process of purification, and raises the proportion of chlorine in the chlorohydrate of cetene by $\frac{1}{2}$ to 1 p. c.

Aqueous potash easily removes hydrochloric acid from the compound, producing at the same time, slender needle-shaped crystals, which melt below 30°, distil without decomposition below 300°, and are insoluble in water : doubtless oxide of cetylene, $C^{32}H^{32}O^2$ (Carius).

Palmitate of Methyl.

$$C^{34}H^{34}O^4 = C^2H^3O,C^{32}H^{31}O^3.$$
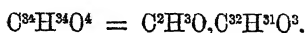
BERTHELOT. *N. Ann. Chim. Phys.* 41, 440.

Methyl-palmitic ether. Palmitinformester.

Obtained by heating palmitic acid to 200°—250° in a sealed tube. It forms crystals which melt at 28° and solidify at 22°.

From margaric acid, wood-spirit, and oil of vitriol, Laurent (*Ann. Chim. Phys.* 65, 287) obtained *margarate of methyl, methyl-margaric acid*, or *margarate of methylene*, in long, pearly, four-sided needles, fusible and capable of being distilled. The melting point of these crystals is stated by Hanhart (*Compt. rend.* 47, 230) to be 27·5°.

Cyanide of Cetyl.

$$C^{34}H^{33}N = C^{32}H^{32}, HCy.$$
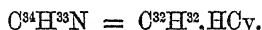
KÖHLER. *Zeitschr. für die gesammten Wissenschaften, J.* 322.
BECKER. *Ann. Pharm.* 102, 209; *J. pr. Chem.* 72, 126; *Chem. Centr.* 1857, 486; *N. Ann. Chim. Phys.* 52, 340.
HEINTZ. *Pogg.* 102, 257; *J. pr. Chem.* 72, 173; *Chem. Centr.* 1857, 684.

Cyancetylafer. — Not known in the pure state.

When 34 grs. cetylene-sulphate of potash and 10 grs. pure cyanide of potassium are very intimately triturated together, with the help of a little alcohol, and, after drying, are heated for several hours to 200°, the two substances melt together to a dark-brown buttery mass. This mass is boiled with ether, the ether distilled off, and the residue dissolved in a small quantity of warm ether, which on cooling deposits crystals of a mixture of cetylic ether and cetylic aldehyde (p. 349), a further quantity being precipitated on addition of absolute alcohol. The mother-liquor, when evaporated, leaves a brown oil, which boils without decomposition at a temperature above 300° and when treated with potash-hydrate, yields margaric acid C³⁴H³⁴O⁴. This, according to Heintz, is cyanide of cetyl.

Köhler heated a mixture of cetylene-sulphate of potash and cyanide of potassium (containing free potash) in an oil-bath to 140° for six or eight hours, the mass then melting together and giving off ammonia. The ethereal solution deposited a neutral, coloured fat, melting below 40°, not saponifiable by boiling potash-ley,—and crystals, melting at 53°, and solidifying again to a crystallo-granular mass, which was nearly insoluble in cold alcohol, and when boiled with alcoholic potash, gave off ammonia and yielded a fatty acid melting at 54·3° to 55°. These crystals are regarded by Köhler as cyanide of cetyl; according to Heintz, however, they contain but little of that compound, but a large quantity of a fatty acid resulting from the action of the free alkali (or of cetylic ether and cetylic aldehyde? Kr.).

Becker boiled iodide of cetyl for several days with alcoholic cyanide of potassium, distilled off the alcohol, and treated the residue with hot water, which separated an oil still brown and contaminated with a fatty acid (margaric acid, according to Becker), which crystallised first from the solution in boiling alcohol. By further evaporation, yellow crystals were obtained, which Becker regarded as cyanide of cetyl. These crystals melt irregularly, one part sooner than the rest, and solidify to an indistinctly crystalline mass. They are insoluble in water, easily soluble in ether and in hot alcohol, and contain 77·2 to 78·6 p. c. C., 13·1 to 13·3 H., and 5·4 N. According to Becker, they are still contaminated with margaric acid (but obtained from alkaline solution, Kr.), and when boiled with alcoholic potash, yield the potash-salts of several fatty acids, which could not be completely separated.

Ethyl-cetylic Ether.

$$C^{36}H^{38}O^2 = C^4H^5O,C^{32}H^{33}O.$$
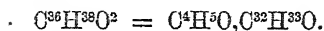
G. Becker. *Ann. Pharm.* 102, 219.

Ethylate of sodium ($C^4H^5NaO^2$) is boiled with iodide of cetyl and alcohol as long as iodide of sodium continues to separate; the foreign admixtures are removed by distillation and washing with water; and the ethyl-cetylic ether is left to crystallise from alcohol.

Laminæ melting at 20°. — Easily in alcohol and ether.

							Becker.
36 C		216		80·00			80·59
38 H		38		14·08			13·61
2 O		16		5·92			5·80
$C^4H^5O,C^{32}H^{33}O$		270		100·00			100·00

Acetate of Cetyl.

$$C^{26}H^{36}O^4 = C^4H^3O^3,C^{32}H^{33}O.$$
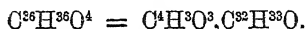
G. Becker. *Ann. Pharm.* 102, 220.
Berthelot. *N. Ann. Chim. Phys.* 56, 71.

Celytic acetate. Cetyl-acetic ether. Ethal acétique. Essigsäure-Cetyläther. Essigcetylester.

Formation and Preparation. 1. Ethal is treated with acetic acid and oil of vitriol or hydrochloric acid; the product is precipitated by water; the separated oil dissolved in ether; and the solution left to evaporate (Becker). — 2. When ethal and acetic acid are heated together for several hours in a sealed tube to 200°, a neutral compound is formed, which cannot be separated from the excess of ethal, and is slowly decomposed by hydrate of lime at 100°, into ethal and acetic acid (Berthelot, p. 347).

Oil, which solidifies in the crystalline form at low temperatures, and melts again at 18·5° (Becker). Volatile without decomposition. Mixes with *ether*.

							Becker.
36 C		216		76·05			76·01
36 H		36		12·67			13·01
4 O		32		11·28			10·98
$C^4H^3O^3,C^{32}H^{33}O$		284		100·00			100·00

Palmitate of Ethyl.

$$C^{36}H^{36}O^4 = C^4H^5O,C^{32}H^{31}O^3.$$
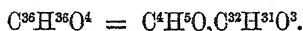
Fremy. *Ann. Pharm.* 36, 46.
H. Schwarz. *Ann. Pharm.* 60, 69.
Heintz. *loc. cit.* (pp. 343, 344).

MASKELYNE. *Chem. Soc. Qu. J.* 8, 11 ; *J. pr. Chem.* 65, 287.
BERTHELOT. *N. Ann. Chim. Phys.* 41, 434, and 440.

Ethylic Palmitate. Ethylpalmitic ether. Palmitinsäure Æther. Palmitin-vinester.

Formation and Preparation. 1. By heating palmitic acid with alcohol and oil of vitriol, or hydrochloric acid (Frémy, Heintz). — 2. By heating alcohol with excess of palmitic acid to 200°—250° (Berthelot). — 3. By heating common ether with palmitic acid to 360° for nine hours (Berthelot).

Properties. Beautiful prisms (Frémy) ; crystallises from dilute alcohol between 5° and 10°, in long flat needles (Heintz). Hard and brittle (Maskeleyne). Melts at 21° (Frémy) ; between 21·5° and 22° (Berthelot); at 24·2° (Heintz) ; at 25° (Maskelyne), and solidifies to a laminated crystalline mass (Heintz) ; at 18° (Berthelot); at 21° (Schwarz). Distils without alteration (Maskelyne). Has a slightly ethereal odour. Not attacked by dilute *nitric acid.*

			Frémy.		Schwarz.		Heintz.		Maske-lyne.
36 C	216	..	76·06	....	75·39	....	75·42	....	75·98	.... 75·87
36 H	36	....	12·68	....	12·53	....	12·66	....	12·69	.... 12·82
4 O	32	....	11·26	....	12·08	....	11·92	....	11·33	.... 11·31
C^4H^5O,$C^{32}H^{31}O^3$	284	....	100·00	....	100·00	....	100·00	....	100·00	.... 100·00

Margaric ether was examined by Laurent (*Ann. Chim. Phys.* 65, 297), Varrentrapp (*Ann. Pharm.* 35, 65), Bromeis (*Ann. Pharm.* 42, 53), Anderson (*Ann. Pharm,* 63, 377), and Hanhart (*Compt. rend.* 47, 230). It melts at 22° (Varrentrapp. Hanhart), at 21·5° (Bromeis).

Monopalmitin.

$$C^{38}H^{38}O^8 = C^6H^7O^5,C^{32}H^{31}O^3.$$
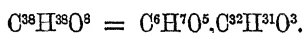
BERTHELOT. *N. Ann. Chim. Phys.* 41, 238; *Chim. organ.* 2, 75.

Formation and Preparation (p. 358). — In like manner, by heating equal parts of margaric acid and glycerin to 200° for 21 hours, or to 100° for 106 hours, Berthelot's *monomargarin* is obtained, which scarcely differs from monopalmitin.

Properties. White needles or short microscopic prisms, which, after drying in vacuo, melt at 61°, and solidify at 45°. They exhibit in fusion and solidification the peculiarities of terstearin (vii, 245), which are also manifested very strongly by monomargarin. After fusion and re-solidification, they melt at 58°.

					Berthelot.		
						a.	b.
38 C	228	... .	69·09	....		67·8	69·50
38 H	38	... ...	11·52	.....		11 8	11·75
8 O	61	. .	19 39	. . .		20·4	18 75
$C^6H^7O^5,C^{32}H^{31}O^3$	330	. .	100·00	... ...		100·0	100·00

b is Berthelot's monomargarin.

Bipalmitin.

$$C^{76}H^{10}O^{12} = C^6H^8O^6,2C^{32}H^{31}O^3.$$
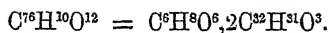
BERTHELOT. *N. Ann. Chim. Phys.* 41, 240 ; *Chim. organ.* 2, 76.

Dipalmitin.

Formation and Preparation (p. 359).

Microscopic thin plates and needles, melting at 59°, and solidifying again in the waxy form at 51°.

					Berthelot.
70 C	420	....	71·67	....	70·4
70 H	70	....	11·94	....	12·0
12 O	96	....	16·39	....	17·6
$C^6H^8O^6,2C^{32}H^{31}O^3$..	586	....	100·00	....	100·0

Terpalmitin.

$$C^{102}H^{98}O^{12} = C^6H^5O^3,3C^{32}H^{31}O^3.$$
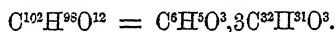
PELOUZE & BOUDET. *Compt. rend.* 7, 665 ; *Ann. Chim. Phys.* 69, 46 ; *Ann. Pharm.* 29, 42,

STENHOUSE. *Ann. Pharm.* 36, 50.

BROMEIS. *Ann Pharm.* 42, 48.

STHAMER. *Ann. Pharm.* 43, 335.

ILJENKO & LASKOWSKY. *Ann. Pharm.* 35, 87.

v. BORCK. *J. pr. Chem.* 49, 395 ; *Chem. Gaz.* 1850, 309 ; *Pharm. Centr.* 1850, 555.

DUFFY. *Chem. Soc. Qu. J.*, 5, 209 ; *J. pr. Chem.* 57, 346.

BERTHELOT. *N. Ann. Chim. Phys.* 21, 240 ; *Chim. organ.* 2, 76.

MASKELYNE. *Chem. Soc. Qu. J.* 8, 7 ; *J. pr. Chem.* 65, 291.

Tripalmitin.

Chevreul distinguished the fat yielded by the saponification of margaric acid as *Margarin*, without however having succeeded in isolating it completely. The products afterwards described by Pelouze & Boudet and others, sometimes as margarin, sometimes as *Palmitin* (by Borck as *Stillistearin*) may be regarded as essentially consisting of terpalmitin ; the true composition of this body was however first established by Berthelot.

Occurrence. In the fats which, when saponified, yield palmitic acid (p. 352), and glycerin. — Formation p. 359.

Preparation. 1. One pt. monopalmitin, and 8 to 10 pts. palmitic acid are heated for eight hours to 250°—270°, and the product is purified with ether and lime, as described at page 359 (Berthelot). Monomargarin similarly treated with margaric acid, yields Berthelot's *Termargarin.*

2. *From Palm-oil.* The oil is strongly pressed between linen to separate the fluid portion, and the residue is treated six or seven times

with boiling alcohol, which removes free palmitic and oleic acids, and leaves palmitin undissolved. This product is recrystallised six or seven times from ether (Stenhouse). Crude palm-oil does not yield colourless palmitin by recrystallisation; but on exposing it to the air, decoloration takes place with facility (Schwarz, *Ann. Pharm.* 60, 72). — 3. *From the solid fat of Stillingia sebifera.* — The melted fat is mixed with ether-alcohol; the mixture is strongly pressed; the press-cake is several times subjected to the same treatment, and the residue is repeatedly crystallised, first from ether-alcohol, then from ether, till the melting point no longer rises (Maskelyne; v. Borck).

Palmitin is likewise obtained from the wax of *Myrica cerifera* (p. 394), by boiling it with alcohol, and recrystallising the undissolved portion from hot ether, with help of animal charcoal.

When peeled Limburg cheese is well boiled with alcohol of sp. gr. 0·825, and the fat which separates on cooling the solution and distilling off the alcohol, is repeatedly crystallised, white flocks of the size of hemp-seed crystallise out, consisting of microscopic, silky needles, melting at 53°, and solidifying at 41°, to a translucent fat with shining surface. These, according to Iljensko & Laskowsky, consist of margarin; they contain 75·51 p. c. C., 12·25 H., and yield by saponification an acid which melts at 60° or 61°, and solidifies to a waxy mass at 57° or 58°.

Properties. Neutral fat melting at 61°, and solidifying to a wax at 46° (Berthelot). Small crystals having a pearly lustre (Maskelyne). When melted, it exhibits the peculiarities of terstearin (*q. v.*, also vii, 245), inasmuch as it first melts at 46°, solidifies again when further heated, then melts temporarily at 61·7°, and permanently at 62·8°(Duffy). It melts temporarily at 50·5°, permanently at 66·5° (Maskelyne).— The melting-point is 48° (Stenhouse, Bromeis); 60° (v. Borck); the solidifying point 45·5° (Duffy); 49° (Chevreul, Maskelyne); 50° (Pelouze & Boudet). — Termargarin melts at 60°, solidifies at 52° (Berthelot). — Terpalmitin solidifies to a waxy, translucent, hard, and brittle mass (Stenhouse, Maskelyne).

					Stenhouse.
102 C	612	... .	75·92	....	75·68
98 H	98	....	12·16	... ...	12·18
12 O	96	. ...	11·92	....	12·14
$C^6H^5O^3,3C^{32}H^{31}O^3$	806	....	100·00	....	100·00

	v. Borck.		Berthelot.		Maskelyne.
			a.	*b.*	
102 C	75·41	....	74·9	73·8	76·12
98 H	12·13	....	12·4	12·0	12·10
12 O	12·46	....	12·7	14·2	11·78
$C^6H^5O^3,3C^{32}H^{31}O^3$	100·00	....	100·0	100·0	100·00

a is Berthelot's terpalmitin; *b* his termargarin. — The acid separated from the soap, melted, in the case of Chevreul's margarin from human fat, at 51°, in that of Stenhouse's terpalmitin and Pelouze & Boudet's margarin, at 60°. Palmitin, which melts at 60°, is still impure, inasmuch as the acid separated from it melts, after recrystallisation, at 62°.

Terpalmitin yields acrolein by *distillation* (Stenhouse). — It is not so easily saponified by potash-ley as olein (Maskelyne) see *Olein.* — It is

decomposed by *alcoholic* acetic acid at 100° in 106 hours (Berthelot, p. 359).

Nearly insoluble in *alcohol,* or only slightly soluble in boiling absolute alcohol, but easily in *ether* (Stenhouse). 100 pts. boiling absolute alcohol, of sp. gr. 0·795 dissolve 21·5 pts. margarin (Chevereul).

Butyrate of Cetyl.

$$C^{40}H^{40}O^4 = C^{32}H^{33}O,C^8H^7O^3.$$

BERTHELOT. *N. Ann. Chim. Phys.* 56, 71.

Cetyl-butyric ether. Ethal butyrique. Buttercetylester.

When ethal is heated with butyric acid in a sealed tube for 8 or 10 hours to 200°, a compound of the two bodies is formed which may be separated from the excess of butyric acid by agitation with aqueous carbonate of potash and with ether. The butyrate of cetyl taken up by the ether cannot be completely separated from the excess of ethal, since it dissolves too readily in alcohol.

Neutral; much more fusible than ethal; volatile, without decomposition, when small quantities of it are heated. It is slowly decomposed by potash at 100°. — Mixes in all proportions with ether.

Succinate of Cetyl.

$$C^{72}H^{70}O^8 = 2C^{32}H^{33}O,C^8H^4O^6.$$
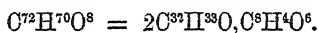
TÜTTSCHEFF. *Socoloff & Engelhardt's* (Russian) *J. f. Chem.* 3, 44, and 337; *Rép. Chim. pure,* 2, 463; *Zeitschr. Chem. Pharm.* 4, 59; *Kopp's Jahresb.* 1860, 405.

Cetyl-succinic ether. Bernsteinsaures Cetyl. Bernsteincetylester.

When a mixture of 1 at. succinic acid and 2 at. ethal is heated in an air-bath for 15 hours, a uniform mass is produced, which may be purified by washing with aqueous carbonate of soda, and repeated crystallisation from warm ether-alcohol.

Fine, white laminæ, which melt at 58°. — Blackens with oil of vitriol. Decomposed by potash into ethal and succinic acid.

Slightly soluble in *alcohol,* more easily in *ether.*

Amyl-cetylic Ether.

$$C^{42}H^{44}O^2 = C^{10}H^{11}O,C^{32}H^{33}O.$$
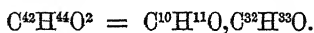
G. BECKER. *Ann. Pharm.* 102, 220.

Obtained, like ethyl-cetylic ether, by the use of amylate of sodium, iodide of cetyl and fusel-oil. Resembles ethyl-cetylic ether. Melts at 30°.

							Becker.
42 C	......	252	....	....	80·77	....	79·65
44 H	......	44	....	14·10	....	13·84
2 O	......	16	......	5·13	....	6·51

$C^{10}H^{11}O,C^{32}H^{33}O$ .. 312 .... 100·00 .... 100·00

Palmitate of Amyl.

$$C^{42}H^{42}O^4 = C^{10}H^{11}O,C^{32}H^{31}O^3.$$
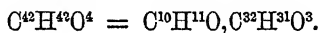
DUFFY.   *Chem. Soc. Qu. J.* v. 314; *J. pr. Chem.* 58, 363; *Lieb. Kopp's Jahresb.* 1852, 514.

BERTHELOT.   *N. Ann. Chim. Phys.* 41, 440.

Amyl-palmitic ether.   Palmitinsaures Amyloxyd.   Palmitinmylester.

Formation and Preparation.   1. Amylic alcohol is heated with excess of palmitic acid in a sealed tube to 200°—300°, and the resulting compound ether is separated from uncombined acid by means of common ether and lime, as in the preparation of palmitin (Berthelot, p. 377.)   Uncombined amylic alcohol may be separated by solution in common alcohol, which dissolves the ether but slightly (Hanhart). — 2. When a solution of 3 at. sodium in amylic alcohol is boiled with 1 at. terpalmitin ($C^6H^5O^3$, $3C^{32}H^{31}O^3$) mixed with a solution of chloride of calcium in fusel-oil, the amylic alcohol expelled by heating, and the residue exhausted with ether, the latter takes up palmitate of amyl (Duffy).

Waxy mass melting at 9° (Berthelot), at 13·5° (Duffy). — *Margarate of amyl* melts at 14°, solidifies at 11°,, and contains 77·43 p. c. C., 13·13 H., and 9·44 O. (Hanhart, *Compt. rend.* 47, 230.)

						Duffy.
42 C	....	252	....	77·30	....	78·60
42 H	....	42	....	12 88	....	12·91
4 O	.. ..	32	....	9·82	... ...	8·49

$C^{10}H^{11}O,C^{32}H^{31}O^3$ .... 326 . ... 100·00 .... 100·00

The alcoholic solution solidifies in the cold to a jelly, without separation of crystals (Duffy).

Bipalmito-mannitan.

$$C^{76}H^{72}O^{14} = C^{12}H^{10}O^8,2C^{32}H^{31}O^3.$$
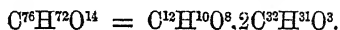
BERTHELOT.   *N. Ann. Chim. Phys.* 47, 323; *Chim. organ.* 2, 190; *Lieb. Kopp's Jahresb.* 1856, 659.

Mannite monopalmitique.   Bipalmitin-mannitanester (xv, 362).

Palmitic acid is heated with mannite in a sealed tube to 120° for 15 to 20 hours; and the fatty layer which floats on the surface and

ether and with excess of slaked lime, heated for 10 minutes to 100°, and then exhausted with ether. If the mannitanide obtained by evaporating the ethereal solution reddens litmus, it must be once more treated with ether and lime.

Solid, white, neutral mass, resembling palmitin, and separating from ether in microscopic crystals. Melts to a wax.

							Berthelot.
76 C	....	456	....	71·25	....	71·6
72 H	....	72	....	11·25	....	11·3
14 O	.. ..	112	....	17·50	....	17·1
$C^{12}H^{10}O^{8},2C^{32}H^{31}O^{3}$	....	640	....	100·00	....	100·0

When *heated* on platinum-foil, it volatilises almost undecomposed, charring only towards the end; the residue burns away. — *Water*, at 240°, decomposes it, after some hours, into mannitan and palmitic acid. — Insoluble in *water*, soluble in *ether*.

Benzoate of Cetyl.

$$C^{46}H^{38}O^4 = C^{32}H^{33}O,C^{14}H^5O^3.$$
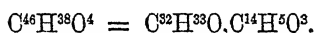
G. BECKER. *Ann. Pharm.* 102, 221.
BERTHELOT. *N. Ann. Chim. Phys.* 56, 71.

Cetyl-benzoic ether. Éthal benzoïque. Benzoesäure-Cetyläther. Benzoecetylester.

Formation and Preparation. 1. A mixture of ethal and chloride of benzoyl in equal numbers of atoms is heated till the evolution of hydrochloric acid ceases; and the resulting mass is dissolved in ether, and precipitated with alcohol (Becker). — 2. Ethal is heated with benzoic acid in a sealed tube for 10 hours to 200°; the contents of the tube are intimately mixed with aqueous carbonate of potash, and shaken up with ether — a little caustic potash being added if necessary, till a sample of the ether no longer gives up any acid to water; the liquid is then decanted, and filtered; and the ethereal solution is decolorised with animal charcoal and evaporated. The residue is freed from uncombined ethal by careful boiling with alcohol, not too often repeated, and the benzoic compound is crystallised from ether (Berthelot).

Crystalline scales, melting at 30°. Neutral.

					Becker.		Berthelot.
46 C	....	276	....	79·74	.... 78·91	....	80·1
38 H	....	38	....	10·98	.... 11·58	....	11·0
4 O	....	32	....	9·28	.... 9·51	....	8·9
$C^{32}H^{33}O,C^{14}H^5O^3$	.. ..	346	....	100·00	.... 100·00	.... ..	100·0

Slowly decomposed by *hydrate of lime* at 100° (Berthelot). — Easily soluble in *ether*, slightly in *alcohol*.

Margarate of Capryl.

$$? \; C^{50}H^{50}O^4 \; = \; C^{16}H^{17}O,C^{34}H^{33}O^3.$$
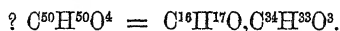
HANHART.   *Compt. rend.* 47, 230 ; *J. pr. Chem.* 77, 5.

Obtained by heating margaric acid with caprylic alcohol (xiii. 183) to 200°. The product is purified from excess of acid with ether and lime, as in the preparation of palmitin (p. 377), and from uncombined caprylic alcohol by treatment with alcohol, which dissolves but a small quantity of the compound ether.

Colourless, inodorous, tasteless. Melts — perhaps when not pure at + 8·5° (Hanhart). Probably a mixture of palmitate and stearate of œnanthyl (Kr.).

Palmitone.

$$C^{62}H^{62}O^2 \; = \; C^{30}H^{32}O^2,C^{32}H^{30}.$$
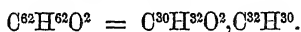
PIRIA.   *Compt. rend.* 34, 140 ; *N. Ann. Chim. Phys.* 34, 281 ; *Ann. Pharm.* 82, 249 ; *J. pr. Chem.* 55, 322.

MASKELYNE.   *Chem. Soc. Qu. J.* 8, 1 ; *J. pr. Chem.* 55, 287.

Ethalone. Discovered as *margarone*, by Bussy, but apparently mixed with stearone (q. v.).

Palmitic acid is distilled with excess of hydrate of lime (Piria), or with one one-fourth of its weight of quick lime (Maskelyne) and the product is purified by repeated crystallisation from boiling alcohol.

Small, white, pearly scales or laminæ. Melts at 84°, and solidifies at 80° to a highly electric mass (Maskelyne).

					Piria. *mean.*		Maskelyne. *mean.*
62 C	372		82·67		82·70		82·65
62 H	62		13·78		13·99		13·88
2 O	16		3·55		3·31		3·47
$C^{62}H^{62}O^2$	450		100·00		100·00		100·00

It resists the action of *nitric acid* and of *potash-ley*, but is attacked and blackened by *nitrosulphuric acid* (Maskelyne). It does not unite with *alkaline bisulphites* (Limpricht, *Ann. Pharm.* 94, 246).

It dissolves in *alcohol* with greater facility as the alcohol is stronger (Piria). Easily soluble in benzol (Maskelyne).

Palmitamide.

$$C^{32}NH^{33}O^2 \; = \; C^{32}AdH^{31},O^2.$$
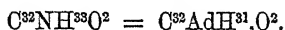
H. CARLET.   *Par. Soc. Bull.* (1859), 1, 75 ; abstr. *Lieb. Kopp's Jahresb* 1859, 366.

The *margaramide* which Boullay obtained by the action of ammonia on olive-oi appears to belong to oleamide.

Palmitate of ethyl is heated with alcoholic ammonia for twenty to twenty-five days in a sealed tube immersed in a salt-bath, and the product is purified by recrystallisation from hot alcohol, and repeated washing with cold ether.

Melts (or solidifies) at 101·5°. By heating in a sealed tube with alcoholic potash, it is resolved into palmitic acid (solidifying at 59·5°) and ammonia.

								H. Carlet.
32 C		192		75·29		75·26
N		14		5·49		5·17
33 H		33		12·90		13·52
2 O		16		6·32		6·05
$C^{32}NH^{33}O^2$		255		100·00		100·00

Tercetylamine.

$$C^{96}NH^{99} = 3C^{32}H^{33},N.$$
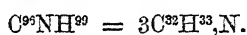
FRIDAU. *Ann. Pharm.* 83, 25.

Tricetylamine.

Formation and *Preparation.* Iodide of cetyl is not decomposed by aqueous ammonia, or by passing ammonia-gas into its alcoholic or ethereal solution; but in contact with ammonia-gas between 150° and 180°, it deposits iodide of ammonium; and by passing the gas through it for several hours it is converted into tercetylamine. The product is purified by re-melting it in water, and crystallising from boiling alcohol :

$$3C^{32}H^{33}I + 4NH^3 = C^{96}NH^{99} + 3NH^4I.$$

Fine white needles, slightly yellowish in the mass when dry. Melts at 39°, and solidifies slowly to a crystalline mass at 33°.

							Fridau.
96 C		576		83·60		83·49
99 H		99		14·37		14·49
N		14		2·03		
$C^{96}NH^{99}$		689		100·00		

Tercetylamine unites with *acids.* Its salts are all insoluble in water, but may be crystallised from boiling alcohol and ether.

Hydrochlorate of Tercetylamine. — Shining needles, which melt in boiling water and float on it as an oil. Less fusible than tercetylamine, but more soluble than the latter in boiling alcohol.

Chloroplatinate. — An alcoholic solution of bichloride of platinum, added to an alcoholic solution of hydrochlorate of tercetylamine, throws down a cream-coloured powder, insoluble in water, and but slightly soluble in alcohol.

		Over oil of vitriol.			Fridau. mean.
$C^{96}NH^{99},HCl$		712·5		80·76	
2Cl		71·0		8·05	
Pt		98·7		11·19		11·37
$C^{96}NH^{99},HCl,PtCl^2$		882·2		100·00	

Tercetylamine dissolves in boiling *alcohol* and *ether.*

Cetylaniline.

$$C^{44}NH^{39} = C^{12}NH^4(C^{32}H^{33}),H^2.$$
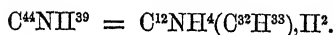
FRIDAU. *Ann. Pharm.* 83, 31.

Cetylophenylamine.

A mixture of iodide of cetyl with a slight excess of aniline deposits, after some days, crystals of hydriodate of aniline, more easily when heated over the water-bath. The product is dissolved in ether, shaken up with water, and converted into hydrochlorate; this salt is decomposed by potash-ley; and the base is crystallised from boiling alcohol:

$$C^{32}H^{33}I + 2C^{12}NH^7 = C^{44}NH^{39} + C^{12}NH^7,HI.$$
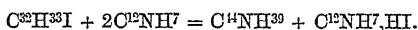
Beautiful silvery scales which melt at 42°, and solidify in the crystalline form at 28°. Neutral to vegetable colours.

				Fridau. mean.
44 C	264	....	83·28	.... 83·29
39 H	39	....	12·30	.... 12·42
N	14	....	4·42	....
$C^{44}NH^{39}$	317	....	100·00	....

Cetylaniline does not precipitate *metallic salts.* — With *iodide of cetyl,* it forms bicetylaniline.

Insoluble in *water.* Its *salts* are insoluble in water, crystallisable, and are precipitated in flocks from their alcoholic solutions by water.

Hydrochlorate and *nitrate of cetylaniline* form shining white needles; the solution of the nitrate blackens when heated.

Chloroplatinate of Cetylaniline. — From a clear mixture of alcoholic bichloride of platinum and alcoholic hydrochlorate of cetylaniline, water throws reddish-yellow crystalline flakes.

				Fridau.
$C^{44}NH^{39}$,HCl	353·5	....	67·57	....
2Cl	71·0	....	13·57	.. ...
Pt	98·7	....	18·86	.... 19·00
$C^{44}NH^{39}$,HCl,PtCl²	523·2	....	100·00	....

Cetylaniline is soluble in *alcohol* and in *ether.*

Bicetylaniline.

$$C^{76}NH^{71} = C^{12}NH^3(C^{32}H^{33})^2,H^2.$$
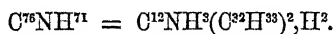
FRIDAU. *Ann. Pharm.* 83, 81.

Bicetylophenylamine.

A mixture of cetylaniline and iodide of cetyl, in equal number of atoms, easily melts when heated, and solidifies at about 110° to hydriodate of bicetylaniline. — The coloured product is purified by (washing with ?) hot alcohol, and decomposed by boiling alcoholic potash; the separated base is well boiled with alcohol, and converted into hydrochlorate; and this salt is crystallised from hot alcohol, by which, however, it is partially decomposed.

The base, which is difficult to separate from the hydrochlorate, resembles cetylaniline, but melts at a lower temperature, and solidifies very slowly. It dissolves with difficulty in boiling alcohol, and crystallises therefrom in rosettes.

From hydrochlorate of bicetylaniline, bichloride of platinum throws down a whitish precipitate, which must be crystallised from ether. It blackens when dissolved in hot alcohol.

				Fridau.
76 C	456·0	61·03		61·78
72 H	72·0	9·64		9·59
N	14·0	1·87		
3 Cl	106·5	14·25		
Pt	98·7	13·21		13·59

$$C^{76}NH^{71},HCl,PtCl^2 \quad 747·2 \quad . \quad 100·00$$

Appendix to the Cetylene-series.

Solid Natural Fats.

1. *Badger-fat.* — Yellowish-white; smells like goose-fat; oily at common temperatures, with a few granules intermixed. At 9°, it becomes white, and of the consistence of salve. Yields a beautiful white soda-soap (Joss). Contains volatile acids, apparently valerianic, capric, and caprylic (Redtenbacher, *Ann. Pharm.* 59, 56).

2. *Fats from various species of Bassia.* — The butter of *Bassia latifolia* (*Handbuch* viii. *Phytochem.* 64) is yellowish, but become colourless by exposure to light; it is of buttery consistence, and sp. gr. 0·958. It softens at 24°, and melts between 27° and 29°. Nearly insoluble in alcohol of sp. gr. 0·84, somewhat soluble in absolute alcohol, easily in ether. Yields by saponification, glycerin, stearic acid (Hardwick's bassic acid), oleic acid, and a third acid melting between 55° and 56° (74·53 p. c. C., 12·65 H.), probably a mixture (Hardwick, *Chem. Soc. Q. J.* 2, 231; *Ann. Pharm.* 72, 268). The last-mentioned acid is, according to Heintz, palmitic acid, containing from 10 to 20 p. c. myristic acid. — *Galam-* or *Bambouc-butter* obtained, according to some, from *Elaïs guinensis*, according to others, from a sapotaceous plant, perhaps *Bassia longifolia*, or *B. butyracea*, is prepared by thoroughly boiling the fruits with water; it is solid, has a mild and slightly aromatic taste, and is perfectly saponifiable (Vauquelin, *J. Pharm.* 16, 53). It is of a dirty reddish-white colour, translucent, of unctuous consistence, faint odour, and distinct cacao taste. After fusion, it becomes opaque and viscid at 29°, and perfectly solid at 21¼°. It is nearly insoluble in cold alcohol

of sp. gr. 0·818, requires more than 40 pts. of boiling alcohol to dissolve it, and separates out almost completely on cooling. It dissolves easily in cold ether, with the exception of a portion which dissolves only on heating, and separates out again as the liquid cools. From solution in boiling acetic ether, the greater part separates, on cooling, in a mass, which does not melt below 26° (Guibourt, *J. Chim. méd.* 1, 175 ; *Mag. Pharm.* 13, 136). It dissolves completely in boiling oil of turpentine. Appears to contain free glycerin. — Probably identical with the preceding is *Illipe-* or *Mahwah-butter,* likewise from a Bassia, which melts at about 25°, and solidifies to a greenish-yellow granular mass at 22°. It contains stearin (O. Henry, *J. Pharm.* 21, 503 ; *Ann. Pharm.* 18, 96), and olein (Pelouze & Boudet, *Ann. Pharm.* 29, 43.) — The *Shea-butter* of West Africa appears to belong to this place; it is greenish-white, softens at 35°, melts at 43° ; dissolves for the most part in boiling alcohol, and crystallises on cooling; also in ether, and crystallises therefrom. By saponification and decomposition of the soap, it yields an acid which separates in pearly scales, melts at 61·1°, and forms a silver-salt, containing 54·71 p. c. C., 8·98 H., 27·83 Ag., and 8·48 O. (Thomson & Wood, *Phil. Mag.* 34, 350; *J. pr. Chem.* 47, 237). — H. L. Buff (*Epist. Communication*) obtained from shea-butter, stearic acid melting at 69·2°, and oleic acid, but no palmitic acid.

Beef-fat, see *Ox-fat.*

3. *Behen-oil.* — From the seed of *Moringa oleïfera* (*Handbuch* viii. *Phytochem.* 12). Pale yellowish-white, of sp. gr. 0·912; liquid at a summer heat of 25°, viscid at 15°, solid in winter. Inodorous ; neutral ; turns rancid but very slowly on exposure to the air, even at a somewhat elevated temperature. Its taste is agreeably sweet and perfectly mild, or, according to some statements, sharp and bitter. By prolonged boiling with potash-ley, it is completely saponified, yielding oleic acid, margaric acid, Mulder's behenic acid ($C^{44}H^{44}O^4$), and an acid melting at 83° (Mulder & Volckel, *J. pr. Chem.* 39, 351). See compounds containing 44 at. C. — Different from this is Walter's behen-oil from *Moringa aptera,* which yields, by saponification, stearic, margaric, benic (p. 365), and moringic acids (see *Oleic acid*), (Walter, *Compt. rend.* 22, 143 ; *Ann. Pharm.* 60, 271).

4. *Bog-butter.* — A fat of unknown origin found in the peat-bogs of Ireland. — It is very light, whitish, and has a faint odour. Melts at 45° (Brazier), at 51° after recrystallisation (Luck), at 52·7° (Brazier). Soluble in alcohol, with the exception of certain impurities. Has an acid reaction. Contains 73·84 p. c. C., 12·43 H., and yields a small quantity of acrolein when heated (Luck). The acid separated from the soap melts at 54°, and solidifies to a non-crystalline mass at 51°, but is still impure. From its lead-salt, ether extracts a hydrocarbon and traces of a soluble lead-salt; and the residue yields, by decomposition, an acid ($C^{33}H^{33}O^4$ according to Luck) containing 75·05 p. c. C., 12·56 H.; the baryta-salt 59·65 p. c. C., 9·62 H., 7·72 O., and 23·01 BaO.; silver-salt, 53·45 p. c. C., 8·61 H., 6·68 O., and 31·26 AgO. (Luck, *Ann. Pharm.* 54, 125). Probably, therefore, palmitic acid ; the melting point of the pure acid is not given (Kr). — Brazier obtained an acid (his *olimnodic acid*) melting at 53°, crystallising from alcohol in white crystals, and having the formula of palmitic acid (Brazier, *Chem.*

Gaz. 1852, 375 ; *Lieb. Kopp's Jahresber.* 1852, 520.) See also Heintz (*Pogg.* 92, 600).

5. *Fat of Brindonia indica.* — This fat cannot be obtained from the dried seeds by pressure, unless they have been previously softened by steam ; but it may be extracted by solvents. — It is nearly white, melts at 40°, dissolves slightly in hot, but is insoluble in cold alcohol. Saponifiable. Contains olein and terstearin, which latter may be obtained from the fat by recrystallisation and pressure (Bouis & Pimentel, *Compt. rend.* 44, 1355 ; *J. pr. Chem.* 73, 176).

6. *Butter.* — The butter of cows' milk, purified as directed at page 92, vol. x, and melted, solidifies at 26·5°, its temperature rising at the same time to 32°9 ; at 17°, the oily portion separates from the solid fat, which crystallises in the granular form (Chevreul). It contains the glycerides of butyric, caproic (caprylic, according to Lerch), capric, margaric, stearic, and oleic acids, a non-acid, odorous, aromatic principle, and often a small quantity of free butyric acid, in which case it reddens litmus (Chevreul, *Ann. Chim. Phys.* 22, 366). The solid acids of butter are the myristic, palmitic, stearic, and arachidic acids (Heintz). The oleic acid of butter is common oleic acid (Gottlieb, Heintz ; — contrary to the statement of Bromeis, *Ann. Pharm.* 42, 46) ; nevertheless, butter likewise contains an oleic acid of lower atomic weight (Heintz). Butter contains 2 p. c. glycerides of volatile acids, 68 p. c. margarin, and 30 p. c. olein (Gottlieb). Summer butter contains relatively larger proportions of olein ; winter butter of stearin (Braconnot, Boussingault, *N. Ann. Chim. Phys.* 8, 96). Butter enclosed in a sealed tube with 2 vol. concentrated alcoholic ammonia, and heated in a salt-bath for 15 or 20 days, forms a solid mass, which melts between 30° and 40°, may be brought, by repeated crystallisation, to the melting (or solidifying) point, 93·5°, and has then the composition of palmitamide (74·01 p c. C., 12·97 H., 4·94 N.), but yields, by decomposition, an acid melting at 52° (Carlet, *Par. Soc. Bull.* 1, 76).

Butter from Human milk appears, from an approximate analysis, to have the same constituents as that from cows' milk (Chevreul, *Ann. Chim. Phys.* 23, 28 ; *Recherches,* 397). — *Butter from goats' milk,* in addition to butyrin, caproin, and perhaps caprin, likewise contains hircin (x, 90) ; hence the different odour of the milk (Chevreul). — *Butter from sheep's, asses', and mares' milk,* appears to contain more olein than that from the milk of cows and goats ; the butter of human milk seems to consist entirely of oil (Braconnot).

7. *Cacao-butter.* From the seeds of *Theobroma Cacao* (*Handbuch* viii. *Phytochem.* 30). White, or yellowish white, nearly as solid as muttonfat ; sp. gr. 0·8916 (Busson) ; 0·91 (Brandis) ; melts at 29° (Pelouze & Boudet) ; at 30° (Stenhouse) ; above 30° (Boussingault) ; at 29·5° to 30°, and solidifies at 23·5° (Specht & Gossmann, Boussingault). After melting it becomes turbid at 23°, opaque at 22°, and acquires at 21·5° the thickness of solidified olive-oil, the temperature, at the instant of complete solidification, rising to 24° (Guibourt & Henry, *J. Chim. méd.* 1, 238). Smells slightly of cacao, and has a mild taste. Dissolves in hot alcohol of sp. gr. 0·818, but only ½ p. c. remains dissolved on cooling. It dissolves abundantly in acetic ether, and still more easily

2 c 2

in common ether, even when cold (Guibourt, *J. Chim. méd.* 1, 177), — Contains 75·2 p. c. C., and 11·9 H. (Boussingault, *Ann. Pharm.* 21, 20).

Cacao-butter yields by saponification, glycerin, oleic acid, stearic acid, and a small quantity of palmitic acid (Stenhouse; Specht & Gössmann). The mixture of acids separated from the soap melts at 51° (Stenhouse). — The liquid portion of cacao-butter contains drying oil; the solid portion is a fat melting at 29°, and composed of olein and stearin in definite proportions (Pelouze & Boudet). By recrystallising cacao-butter from ether, warty crystals are obtained, consisting of Mitscherlich's *cacao-stearin.* On melting and cooling this substance, crystallisation begins at 25°, and becomes more abundant at 23·5°, the temperature then rising to 31°. Cacao-stearin yields, by saponification, a fatty acid melting at 65°, and oleic acid. A second fat of cacao-butter melts more easily than the butter itself, and yields, by saponification, a solid and a liquid volatile acid (A. Mitscherlich, *Kopp's Jahresber.* 1859, 594).

8. *Calf- or Veal-fat.* — White; softer than beef-suet; greasy to the touch; has a sharp, disagreeable odour. Begins to melt at 52°. The soda-soap is brownish-yellow, moderately hard, and nearly inodorous (Joss).

9. *Camel-fat.* — From the hump. Yellowish-white; softer than beef-suet; begins to melt at 22·5°. The soda-soap is brownish-white, inodorous, and becomes very hard (Joss).

10. *Fat of Cantharides.* The fat extracted by ether is buttery, somewhat granular, green, with acid reaction, and the odour of cantharides. Melts at 34°, solidifies at 32°. Yields, by saponification, a trace of volatile acid, also palmitic acid, oleic acid, and a small quantity of stearic acid. These, according to Gossman, are present as acid glycerides (Gössman, *Ann. Pharm.* 86, 317; 89, 123).

11. *Carapa-oil.* — From the seed of *Carapa guianensis.* Colourless, viscid, nearly solid (Richard). When expressed in the warmth of the sun, it becomes solid at 4° and melts at 10° (Boullay). Tastes very bitter. When exposed to the air, it becomes yellowish, rancid, and of the consistence of butter. It is anthelmintic (H. Richard, *J. Chim. méd.* 6, 38; *Br. Arch.* 34, 146). It may be freed from bitter principle by repeated boiling with water, or by hot acetic acid (Boullay, *J. Pharm.* 7, 293). Sparingly soluble in alcohol, easily in ether (Cadet, *J. Pharm.* 5, 49).

12. *Chinese* or *Vegetable Tallow.* From the berries of *Stillingia sebifera* (*Handbuch* viii. *Phytochem.* 24), which contain a tallowy fat in the husk, and a liquid fat in the kernel. It appears to occur in several varieties. *a.* Greenish-white; melts at 44·4°; yields, by saponification, an acid, which, after recrystallisation from alcohol, softens at 61·7°, melts at 67·8°, and forms a silver-salt containing 27·95 p. c. silver; probably a mixture of palmitic (margaric, according to Thomson & Wood) and stearic acids (Thomson & Wood, *Phil. Mag.* [3] 24, 350; *J. pr. Chem.* 47, 239).

b. The commercial tallow forms a light white mass of sp. gr. 0·818 at 12°, destitute of taste and odour (v. Borck). Has a faint odour, and turns brown on exposure to the air (Maskelyne). Melts at 37°

(v. Borck, Maskelyne), solidifies partially at 32° (Maskelyne), 30° (v. Borck), and hardens at 22° (v. Borck), 26° (Maskelyne). The tallow recently melted and cooled again melts at 44°; by expressing the more fusible portion, the melting point of the residue may be raised to 49° (Maskelyne). The fat extracted from the husk by boiling alcohol melts at 40°, and after recrystallisation at 48° (v. Borck). It dissolves in oil of turpentine and in coal-tar oil; in wood-spirit, ether, and alcohol, or in mixtures of these liquids, it dissolves partially at mean temperatures, completely at the boiling heat (Maskelyne). — It has an acid reaction, arising from admixture of acetic or propionic acid. It contains olein and palmitin. The palmitic acid separated from the latter is that which v. Borck described as stillistearic acid. (Maskelyne, *Chem. Soc. Qu. J.* 8, 1; *J. pr. Chem.* 65, 287; v. Borck, *J. pr. Chem.* 49, 395).

13. *Fat of Cocculus-grains.* — From the seeds of *Menispermum Cocculus (Handbuch, viii., Phytochem. 44)*. White, scentless, of mild taste, sp. gr. 0·9. Dissolves in 12 pts. of boiling alcohol, 25 pts. cold alcohol, and in 2⅓ pts. ether (Boullay, *Bull. Pharm.* 4, 21). The fat expressed from the peeled seeds, with aid of heat, melts partially at 22°, completely at 25·5°. It is nearly insoluble in cold, easily soluble in warm alcohol, easily also in ether, whence it crystallises in warty crusts (Crowder, *Phil. Mag.* [4], 4, 21). — Contains oleic and stearic acids, partly free, partly as glycerides (Francis, *Ann. Pharm.* 42, 255). Casaseca & Lecanu found also margaric acid; Crowder likewise observed an acid which melted at a lower temperature than stearic acid (at 56°), perhaps palmitic acid. — When cocculus grains are freed from picrotoxin and colouring matter, by treating them three or four times with alcohol, and the residue is exhausted with warm ether, the ethereal liquid deposits on cooling, or when the ether is distilled off, a white fat, which after recrystallisation from boiling absolute alcohol, forms the *Stearophanin* of Francis. It melts between 35° and 36°; solidifies on cooling to a tough, non-friable, waxy mass having a wavy surface; contains 75·9 p. c. C., 12·2 H., and 11·9 O.; dissolves sparingly in alcohol, easily in warm ether. It yields stearic acid by saponification, and acrolein by dry distillation, but does not agree in melting point with terstearin.

14. *Cochineal-fat.* — Cochineal is exhausted with ether; the ether is evaporated; the residual yellow fat is dissolved in absolute alcohol; the solution cooled; and the fat which then separates is twice re-dissolved in alcohol, or till it has lost its red colour. — White translucent laminæ, melting at 40°, destitute of taste and odour. It is saponified by alkalis. Soluble in ether, and in hot, but not in cold alcohol (Pelletier & Caventou, *Ann. Chim. Phys.* 8, 271). The fat of *Coccus polonicus* crystallises after cooling like spermaceti (Lowitz, *Scher. Ann.* 4, 45); when obtained by extraction with ether, it is reddish-yellow, hard, and brittle, and of repulsive animal odour. It melts at 71·5°, solidifies partially at 55°, completely at 50°, and forms a very hard, white, inodorous soda-soap (Joss, *J. pr. Chem.* 1, 39). It dissolves in less than its own weight of hot alcohol, forming a liquid which solidifies on cooling (Kirchhoff, *Scher. Ann.* 4, 44).

15. *Cocoa-nut oil. Cocoa-fat. Cocoa-butter.* — From the nut of *Cocos nucifera*. The fat obtained by boiling with water, is white,

of unctuous consistence, melts to a thin oil which solidifies again at 16° or 18°, and tastes like butter and cheese. It is less soluble in alcohol of sp. gr. 0·818 than palm oil, but much more soluble than Galam-butter (Guibourt, *J. Chim. méd.* 1, 178). — The fat obtained by cold pressure is greenish-white, moderately firm at 9°, crystalline, melts at 21°, completely at 31°, becomes turbid at 12°, and yields a scentless, hard and white soda-soap (Joss, *J. pr. Chem.* 1, 33). It dissolves readily in cold ether (Lecanu). Compare Trommsdorff (*A. Tr.* 24, 2, 54); Bizio (*J. Pharm.* 19, 456); also ix, 365; xv, 44; and under *Azelaic acid.* — The glycerin of cocoa-nut oil does not differ in any respect from ordinary glycerin (A. W. Hofmann, *Ann. Pharm.* 115, 276).

16. *Coffee-fat.* — Coffee is exhausted with alcohol of 40,° B, and the solution is cooled to − 6°, whereupon part of the fat separates out; the rest may be precipitated by water. White, inodorous, of the consistence of lard; melts at 37·5°; turns rancid on exposure to the air (Seguin, *Ann. Chim.* 92, 13). Contains palmitic acid, and an acid having the composition $C^{24}H^{24}O^4$, more soluble than palmitic acid, but perhaps a mixture (Rochleder, *Wien. Akad. Ber.* 24, 40).

17. *Corpse-fat. Adipocire.*—The fat of a pig which had been buried for 15 years was free from glycerin and ammonia, and contained stearic acid (melting at 79°!), margaric acid melting at 60°, and oleic acid (Gregory, *Ann. Pharm.* 61, 362);—Adipocire of a sheep buried for 16 years contained 94·2 p. c. solid fatty acids, a small quantity of oleic acid, and a trace of volatile acid, but neither ammonia, glycerin, nor cholesterin.—The fat of human bodies, buried for intervals of 6 to 15 years, contained from 97·3 to 97·8 p. c. fatty acids, including palmitic, stearic, and oleic acids. The fat from a fossil bone of *Bison americanus* contained the fatty acids of tallow to the amount of 86·31 p. c., combined with 10·10 p. c. lime (Wetherill, *J. pr. Chem.* 68, 26; *Lieb. Kopp's Jahresber.* 1855, 517. See also *Handbuch,* viii. *Zoochem.* 542).—On distilling portions of a human body which had been buried for 5 years, with aqueous hydrochloric of sp. gr. 1·14, Ludwig and Kromayer (*N. Br. Arch.* 97, 275) saw laminar crystals pass over, having a repulsive odour. These crystals contained free stearic and palmitic acids, and a brown, stinking, sulphuretted oil, not capable of uniting with bases.—See further Embke (*A. Gehl.* 4, 439; Chevreul, *Ann. Chim.* 95, 25; Landerer, *Repert.* 44, 1; H. Muller, *Repert,* 44, 21).

18. *Fat of Cyclicodaphne sebifera.*—Melts at 45°; contains 14 p. c. olein and 85·2 p. c. laurostearin (Gorkom, *Lieb. Kopp's Jahresb.* 1860, 323).

19. *Deer-fat.*—This fat contains two kinds of tallow which can be separated by boiling alcohol. The *undissolved tallow* is white, brittle, scentless, of dull fracture, and sp. gr. 0·968; it softens at 49°, begins to melt at 49·5°, and to solidify at 46·5°. When saponified it yields an acid melting at 35°. It is perfectly insoluble in boiling alcohol of sp. gr. 0·88, slightly soluble in boiling alcohol of sp. gr. 0·83, but separates out almost completely on cooling. It dissolves completely in ether, especially at the boiling heat, and in warmed oil of turpentine. — The *dissolved tallow* separates from the alcoholic solution on cooling, while olein remains dissolved. It resembles the former. Sp. gr. 0·97. Begins to melt at 57°; the acid separated from the soap begins to melt at 53·5°. This tallow is more soluble in alcohol than the former (Joss).

20. *Fat of Diku-bread.*—From the almonds of *Mangifera gabonensis* (*Handbuch* viii. *Phytochem* 19). Obtained by boiling with water and pressing. Resembles cacao-butter. Melts at 30°, or, if it has been extracted with ether, at 33·5°. Contains lauric acid (xv. 43) and myristic acid (xvi. 209), doubtless as glycerides.

21. *Dog-fat.*—Brownish white, with the taste of goose-fat and a faint odour. Begins to melt at 22·5°. The soda-soap is white, hard, and becomes in course of time greenish white and very hard (Joss).

22. *Elephant's fat.*—White or yellowish; soft; nearly inodorous in the fresh state, melting at 28° ; after separation of the liquid portion, it melts at 47·8° ; after repeated crystallisation from alcohol, at 50°. Contains 21·3 p. c. margarin, 78·7 p. c. olein. The liquid fat dissolves sparingly in alcohol, easily in ether. It is not converted into elaïdic acid by nitric acid, and does not dry up. (Filhol & Joly, *Compt. rend.* 35, 393 ; *Lieb. Kopp's Jahresber.* 1852, 519).

23. *Fox-fat.*—Of the colour and hardness of goose-fat at common temperatures, like hog's lard at 9°. Begins to melt at 27° ; perfectly fluid at 54° (Joss).

24. *Goat's fat.*—Contains about 69 p. c. stearin, 26 p. c. margarin, and 5 p. c. olein (Joss, *J. pr. Chem.* 4, 369).

25. *Goose-fat.*—Very pale yellow; melts between 24° and and 26° ; has an agreeable odour. Neutral. Contains, besides stearin and olein, a trace of matter soluble in water (Chevreul). Contains glycerides of the volatile acids, caproic and butyric, and of the fixed acids, stearic, margaric, and oleic (Gottlieb, *Ann. Pharm.* 57, 34).—By pressure at − 2°, it may be resolved into 32 p. c. tallow, melting at 44°, and 68 p. c. slightly coloured oil (Braconnot); Gusserow (*Kastn. Arch.* 19, 71) separated it into ⅓ tallow and ⅔ oil. When the two fats are saponified and the soaps decomposed, the tallow yields acids whose melting points range from 47° to 48°, while the oil yields acids melting between 38° and 39°. When the two mixtures of acids are converted into lead-salts, ether extracts from the lead-salts obtained from the tallow, 31 p. c., and from that yielded by the oil, 63·8 p. c. oleate of lead.

26. *Hare's fat.*—Honey-yellow; smells like linseed-oil varnish; viscid, syrupy and friable at common temperatures. Dries up on exposure to the air. Begins to melt at 26°. Very difficult to saponify, a brown resin separating at the same time. The soda-soap is yellow, light, hard, and has a faint odour (Joss). Contains volatile acids (Redtenbacher).

27. *Hog's lard.*—White; of sp. gr. 0·912 (Brandes & Reiche). Sp. gr. = 0·938 at 15°; = 0·8918 at 50° = 0·8811 at 69°; = 0·8628 at 94°, that of water at 15° being = 1 (Saussure). Melts at 40·5° (A. Vogel); that from the kidneys is perfectly fluid at 30° (Gusserow). As the melted fat solidifies, the temperature rises, sometimes from 26° to 27°, sometimes from 29° to 31° (Chevreul). Has a faint odour, excepting when heated with water. Does not redden litmus.—Contains stearin, margarin, olein, a substance smelling like bile, also chloride of sodium and acetate of soda (Chevreul). Braconnot *Ann.* (*Chim. Phys.* 93, 231)

decomposed it by pressure at 0°, into 62 pts. colourless oil not solidifying at a very low temperatures, and 38 pts. tallow. Gusserow (*Kastn. Arch.* 19, 75), obtained, by pressure at 3°, then at 6° to 8°, 35 pts. tallow melting between 46° and¦48°, and yielding by saponification acids melting between 62° and 65°, together with 65 pts. olein solidifying at + 2°. — The acids separated from hog's lard solidify at 39° (Chevreul). Hog's lard becomes rancid and yellow when exposed to light, even if air be excluded, but does not turn sour unless exposed to the air (A. Vogel). See *Terstearin*. By dry distillation, it yields acrolein (ix. 365) (Buchner), together with a mixture of hydrocarbons containing equal numbers of atoms of carbon and hydrogen (Gerhardt, *N. Ann. Chim. Phys.* 15, 243).—By the pancreatic juice, it is resolved into glycerin and acids melting at 61° (Berthelot). Dissolves phosphorus and sulphur.—Soluble in 36 pts. boiling alcohol of sp. gr 0·816 (Chevreul).—(On the adulterations of hog's lard, see Chateau, *Mulh. Soc. Bull.* 32, 403))

28. *Horse-fat.* — Brownish, of the consistence of turpentine, with a faint, fatty odour. At 9° it acquires the consistence of hog's lard, but a portion remains liquid. — The soda-soap is brown, very hard. and becomes softer by keeping. — The *marrow* of the bones is waxyellow, greasy, unctuous, hardens, and becomes greenish-yellow on exposure to the air. It begins to melt at 65°, and becomes syrupy at 84°. The soda-soap is hard, very white, scentless, and light. — The *neck-fat* is pure white, more solid than hog's lard, contains ¼ stearin and ¾ olein. Begins to melt at 32°. The soda-soap is yellowish, very soft, and greasy (Joss, *J. pr. Chem.* 1, 37).

29. *Human fat.* — That of the kidneys is yellowish, scentless, becomes turbid at 25° after fusion, and solidifies completely at 17°; that from the thighs is yellowish, scentless, perfectly fluid at 15°, depositing tallow only gradually, while a large portion remains liquid (Chevreul). That from the extremities is perfectly fluid between 20° and 22°, and solidifies between 12° and 15°; in other cases, it melted between 15° and 18°, and solidified to a soft mass at 6° or 7°. Between 12° and 15°, it is resolved into olein and stearin (Gusserow, *Kastn. Arch.* 19, 76). — Not acid (Chevreul). — The expressed liquid portion, when left to stand in half-closed vessels, gradually deposits solid fatty acids (Heintz). — Human fat dissolves in 40 pts. alcohol of sp. gr. 0·821 (Chevreul). — It contains oleic, palmitic, and a small quantity of stearic acid, all in combination with glycerin (Heintz). It contains margarin and olein, and a bitter yellowish substance, having the taste and odour of bile; the soap yields also a trace of volatile acids [including caprylic acid (Lerch, *Ann. Pharm.* 59, 57)] (Chevreul). According to Lecanu, it contains a peculiar tallow, having a pearly lustre, and slightly soluble in ether. — The oil expressed from human fat is olein, with a small quantity of another oily fat, the acid of which forms a baryta-salt containing 27 to 28 p. c. baryta, more fusible and more soluble in ether, but less soluble in alcohol than oleate of baryta (Heintz).

30. *Jaguar's lard.* — Orange-yellow; solidifies at 29·5°, a small quantity of oil remaining liquid; has a very unpleasant odour, becoming stronger on saponification. Does not redden litmus. Contains, besides oil and tallow, a yellow, bitter, oily substance, which remains dissolved on precipitating the alcoholic solution with water, and apparently also

a small quantity of acetic acid. Yields by saponification, glycerin having an offensive odour, and an acid solidifying at 36°. Soluble in 46 pts. alcohol of sp. gr. 0·891 (Chevreul).

31. *Japan wax.* — Imported from the East Indian Islands and Japan, also from the West Indies and Brazil, perhaps in several varieties. According to Fr. Nesenbeck (*Repert.* 46, 283), it is obtained in Japan from *Rhus succedanea.* Landerer (*Repert.* 44, 1) regarded it as adipocire. — Large round cakes, about an inch thick, arched and forked on one side ; when exposed to the air, it becomes covered with a white film (Sthamer). Yellowish white; has a somewhat rancid smell and taste, producing irritation in the throat; softer and more unctuous than wax, but more friable, and may be distinguished by its property of crumbling to a coarse powder when chewed. Sp. gr. 0·98 (Muller, Trommsdorff), 0·97 at 19° (Oppermann). Has an acid reaction. When warmed, it first becomes tough, than melts at 47·5° (Trommsdorff), 45° (H. Muller); at 42° and solidifies at 40° (Sthamer). The East Indian variety melts at 50°, and solidifies at 42·5° ; the West Indian melts at 49°, and solidifies at 45° ; the former contains 70·00 p. c. C., 12·07 H. ; the latter 71·88 C., 12·03 H. (Oppermann).

When completely saponified, it yields glycerin, and a hard, compact, friable soap, the acid of which melts at 60° (Oppermann), and consists of palmitic acid free from oleic. The wax purified by recrystallisation from ether contains, on the average, 73·12 p. c. C., 11·85 H. (Sthamer), and according to Berthelot (*N. Ann. Chim. Phys.* 41,242), should perhaps be regarded as bipalmitin (p. 377). · Brandes (*N. Br. Arch.* 17, 288) saponified the wax with alcoholic potash, and regarded the resulting acid as identical with the wax-acid of Hess. — When Japan wax is subjected to dry distillation, acrolein is evolved, and a dark-coloured distillate is obtained, which melts at 49°, does not give up sebacic acid to boiling water, but by solution in potash-ley, salting out, and decomposition of the soap, yields an acid, which, after recrystallisation from alcohol, exhibits the composition and properties of palmitic acid. — The wax oxidised by nitric acid, yields succinic, but no other acid (Sthamer, *Ann. Pharm.* 43, 335). It is easily bleached by chlorine, but the chlorine cannot be subsequently quite removed from it (Trommsdorff, *J. pr. Chem.* 1, 151). It dissolves in 3 pts. boiling alcohol of 96 p. c. ; not in the same liquid when cold; the solution solidifies on cooling to a white fine-grained mass (H. Müller, *Repert.* 14, 25). The solution in hot ether deposits flocks (Oppermann, *Mag. Pharm.* 35, 57; *Ann. Chim. Phys.* 49, 240).

32. *Laurel-fat* or *Bay-fat.* — Obtained by boiling or pressing bay-berries. Yellow-green, granular butter, or thick oil, having an aromatic odour, and bitter aromatic taste. It contains a volatile oil (xiv, 360), laurel- or bay-camphor (xv. 52), laurostearin (xv. 50), a liquid green fat, and a resin. It dissolves perfectly in ether, partially in cold alcohol (Bonastre, *J. Pharm.* 10, 30. — Marsson, *Ann. Pharm.* 41, 329). See also Grosourdi (*J. Chim. méd.* 7, 257, 321 and 385 ; abstr. *Lieb. Kopp's Jahresber.* 1851, 562), who distinguishes between *Stearolaurin* and *Stearolauretin* from laurels.

33. *Mafurra-tallow.* From the seed of a plant indigenous in Mozambique. Yellowish; smells like cacao-butter; melts less easily than beef-fat. Dissolves sparingly in boiling alcohol, easily in ether. Contains olein and palmitin (Bouis & Pimentel, *Compt. rend.* 41, 703 ; abstr. *J. pr. Chem.* 67, 286).

34. *Fat of Maize-seed.* — Occurs in variable quantity, and not in

every variety of maize. — Yellow butter, red in rather thick layers; melts between 22° and 25°; has a faint odour of vanilla; separates on filtering paper into oil and tallow; soluble in alcohol, and in all proportions in ether (Bizio). — The thick yellow oil extracted by ether, dissolves completely in alkaline carbonates, forming a soap; hence it consists of a fatty acid, probably formed from the fat of the seed. Contains 79·68 p. c. C., 11·53 H., and 8·79 O. (Fresenius, *Ann. Pharm.* 45, 127).

35. *Mutton-fat.* — White, scentless at first, but acquires a peculiar odour by exposure to the air. Neutral (Chevreul). Melts at 50° (Arbächer). Solidifies at 37°, the temperature raising to 39°, or at 40°, with rise of temperature to 41° (Chevreul). Consists mainly of stearin, together with palmitin and small quantities of olein and hircin (x, 89) (Chevreul, Heintz). According to Lecanu, it contains, in addition to stearin, a peculiar fat, which melts at 47°, yields by saponification an acid melting at 66°, and is much more soluble in ether than stearin. It contains, besides oleic acid, a liquid acid of lower atomic weight, the baryta-salt of which is taken up by ether before the oleate (Heintz, *Pogg.* 87, 555). From the alcoholic solution, water precipitates mutton-suet, whilst an acid extractive matter remains in solution (Chevreul). Dissolves in 44 pts. boiling alcohol of sp. gr. 0·821 (Chevreul); in more than 60 pts. of (cold) ether (Lecanu). *Comp.* Braconnot (*Ann. Chim.* 93, 274), Nicholson (*Scher. J.* 1, 481.) — *Sheep's marrow* is resolved by pressure at − 2° into 26 pts. solid friable tallow melting at 51°, and 74 pts. oil (Braconnot).

36. *Myrica-tallow, Myrtle-wax.* — Obtained by pressing the berries of *Myrica cerifera* (or *M. cordifolia*, John), with water. — Pale green, translucent, brittle and friable in the cold, of splintery fracture, less extensible when warm than bees-wax. Has an aromatic taste and odour. Sp. gr. 1·0 (John); 1·015 (Bostock); 1·005 (Moore). Melts at 42·5° (John); 43·0° (Bostock); 49° (Chevreul); 47° to 49° (Moore). When purified by treatment with boiling water and cold alcohol, it melts at 47·5°, and contains 74·03 p. c. C., 12·07 H., and 13·70 O. (Lewy, *N. Ann. Chim. Phys.* 13, 448). — Contains a large quantity of palmitic and a small quantity of myristic acid, for the most part in the free state, but to a smaller extent combined with glycerin; no oleic, nor any volatile acid (Moore). According to Chevreul, it yields by saponification, stearic, margaric, and oleic acids. According to Bostock & John, it contains myricin and cerin, besides chlorophyll, odoriferous substances, and traces of salts. — It dissolves in oil of vitriol with yellow, or if heated, with brown colour. — Saponifies easily, forming a very solid, white soap (Cadet, Bostock); the mixture of acids separated therefrom melts at 60° or 61° (Moore). With ammonia it forms an emulsion; with litharge it forms with great facility a hard plaster (Cadet, Bostock).

It dissolves in 20 pts. of hot alcohol, a portion (palmitin, according to Moore), remaining however undissolved, and on cooling ⅘ separates out (Bostock); the solution, formed with aid of heat, solidifies on cooling, and when perfectly cold, is no longer precipitable by water (John). It is nearly insoluble in cold ether, but dissolves in 4 pts. of boiling ether, the solution, as it cools, depositing the greater part of the tallow without colour, and itself retaining a fine green colour

(Bostock). Cold oil of turpentine softens myrica-tallow, and hot oil of turpentine dissolves it to the amount of $\frac{1}{17}$th of its own weight, the solution on cooling, depositing white opaque granules. Fat oils likewise dissolve the tallow with facility (Cadet, *Ann. Chim.* 44, 140 ; Bostock, *Nicholson J. of Natur. Phil.* 4 ; *A. Gehl.* 6, 645 ; John, *Chem. Schrift.* 4, 38 ; Moore, *Sill. Amer. J.* [2], 33, 313 ; *Chem. Centr.* 1862, 779).

37. *Fats of various species of Myristica.* — a. *Nutmeg-butter.* — Obtained by pressing the seeds of *Myristica moschata.* Commercial nutmeg-butter melts at 51° (Uricoechea) at 41° (Ricker). Sp. gr. 0·995 (Ricker). It contains, besides volatile oil (xiv. 389) and nutmeg-camphor (xiv. 389), two solid fats, the larger portion consisting of myristin (xvi. 215) which remains undissolved when the whole is treated with cold alcohol. On evaporating the alcoholic solution, there remains a red, soft fat, which, when distilled with water, gives off a volatile oil, and on subsequent distillation without water, white crystals exhibiting the characters of paraffin. In the retort there remains a black saponifiable mass (Playfair, *Ann. Pharm.* 37. 152 and 163). — Nutmeg-butter is only partly saponified by boiling with potash, half of it remaining in the form of an oil which solidifies on cooling (Bollaert). It dissolves in 4 pts. of boiling alcohol, and only partially in cold ether (Schrader, Lecanu).

The fat obtained from bruised nutmegs by warm pressing has a sp. gr. of 0·998, a pale yellow colour, quickly becoming whitish, and a strong odour of nutmegs. It melts at 45°, and forms warty excrescences when solidified. It makes grease-spots on paper, but slowly and only when warmed. The saturated solution in boiling ether solidifies, on cooling, to a solid coherent crust, whereas the solution of commercial nutmeg-butter remains pulpy. The ethereal solution if evaporated, after the addition of absolute alcohol, deposits rings of crystals (A. Ricker, *N. Jahrb. Pharm.* 19, 17).

The *non-saponifiable fat of nutmeg-butter* is white, crystalline, very fusible, tasteless, and inodorous. It boils at 315·5° without much decomposition, is inflammable, and is converted by nitric acid, with evolution of nitrous gas, into a still crystalline yellow mass, easily saponifiable by alkalis. It is carbonised by oil of vitriol, but is not altered either by hydrochloric acid or by boiling potash-ley. It dissolves sparingly in cold, abundantly in hot alcohol, separating out on cooling ; easily in cold ether and in fixed oils (Bollaert, *Chem. Soc. Qu. J.* 18, 317).

b. *Otoba-fat.* From the fruit of *Myristica Otoba.* — Nearly colourless, buttery, smells like nutmegs when fresh, disagreeably when melted. Melts at 35°. Contains myristin (p. 215), olein, and otobite (Uricoechea, *Ann. Pharm.* 91, 369).

The *Otobite* passes into the soap, and into the precipitate formed by treating the soap with alcoholic magnesia. When the myristic acid separated from this precipitate, is dissolved in alcohol, otobite remains behind, and may be obtained pure and crystallised from hot alcohol or ether. — Large colourless prisms, having a glassy lustre, tasteless and inodorous, melting at 133°, and solidifying in the crystalline, or if more strongly heated, in the amorphous state. It is not volatile, but creeps up the sides of the tube when heated. Insoluble in water.

Contains, on the average, 73·02 p. c. C., 6·40 H., and 20·58 O., agreeing with the formula $C^{24}H^{13}O^5$ (Uricocchea).

Ocuba-wax from *Myristica ocaba, officinalis,* or *sebifera* is yellowish-white, melts at 36·5°, dissolves in boiling alcohol, and contains 74·00 p. c. C., 11·35 H., and 14·65 O. (Lewy, *N. Ann. Chim. Phys.* 13, 449).

c. *Tallow of Myristica sebifera. Virola tallow.* Obtained by boiling the shelled almonds. Yellowish cakes, covered with a thin, pearly, whitish crust, black in the interior, and marked with white, from separation of white groups of crystals. Melts partially at 44°, completely at 50°. Half soluble in ammonia-water, perfectly in alcohol and ether. It is but partially saponifiable, leaving white flocks, soft, tough, and less fusible than the tallow itself (Bonastre, *J. Pharm.* 19, 190; *Ann. Pharm.* 7, 49).

d. *Bichuhyba fat. Becuiba-balsam.* — From the fruit of *Myristica officinalis* s. *Bicuhyba.* Resembles nutmeg-butter, but has a sourish, sharp taste. By agitation with 12 times its weight of absolute alcohol, it is resolved into 45 p. c. of yellowish pulverulent residue, and a solution which, when evaporated, deposits a pale yellow laminated fat. The portion insoluble in cold absolute alcohol, forms when recrystallised from boiling alcohol of 75 p. c.—which leaves behind a brown tenacious mass—a white friable tallow, having a mild taste and no smell, saponifiable, and yielding, by decomposition of the soap, an acid which melts at 40° (Brandes, *Ann. Pharm.* 7, 52). A white-yellow bicuhyba fat melting at 35°, and soluble in boiling alcohol, was found to contain 74·38 p. c. C., 11·12 H., and 14·50 O. (Lewy, *N. Ann. Chim. Phys.* 13, 450). — The fruit of *Myristica off.* yields, by warm pressing, a yellow-brown fat which solidifies immediately, and a larger quantity of it on subsequent exhaustion with ether. This fat melts at 47·5°, and solidifies at 25°; sp. gr. = 0·9559 at 25°. Oil of vitriol colours it brown, and dissolves it with dark red colour; sulphurous acid decolorises it completely. Hot nitric acid renders it more solid, and gives it a bright orange-yellow colour; mercurous nitrate causes it to solidify in the form of *bicuhyba-elaïdin.* It is saponifiable, and yields a friable soap. When this fat is washed successively with water and with alcohol, the water takes up a brown glutinous extract, and the alcohol dissolves fat and resin; the thoroughly washed residue yields, by saponification and decomposition of the soap, volatile acids (one of which is crystallisable), and non-volatile fatty acids, which may be separated by cold alcohol, into a soluble oily portion and an insoluble residue. The soluble portion melts at 17·5° to a brown oil. From the insoluble portion, boiling alcohol extracts bicuhyba-stearic acid, leaving a brown resin undissolved. *Bicuhyba-stearic acid* separates from boiling alcohol in colourless needles, melting at 55°, solidifying at 35°. Oil of vitriol colours it red brown, itself becoming brown-red in half an hour, and afterwards crimson. With soda, baryta, magnesia, and lead-oxide, the acid forms salts, which dissolve in ether and crystallise therefrom; the cupric salt is insoluble in water. The glyceride of this acid may be extracted by boiling alcohol from the fruits previously exhausted with ether, and separates from the cooled solution in white flocks. With potash, it forms a red soap, from which acids precipitate white bicuhyba-stearic acid (Peckolt, *N. Br. Arch.* 107, 285, 108, 14).

The arillus (mace) of *Myristica officinalis* contains a fat, viscid, gold-yellow oil, which may be extracted by ether, and solidifies at $+ 15°$ to a white mass of crystalline stars. Tastes and smells like olive-oil. Does not solidify with nitric acid (Peckolt).

38. *Ox-* or *Beef-fat.* — Pale yellow or white; melts at 47° (Arzbächer); at 39°, and solidifies at 37° (Chevreul). Dissolves in 40 pts. boiling alcohol of sp. gr. 0·821.—Contains more stearin than human fat, more palmitin than mutton fat, and about as much olein as the latter (Heintz). By saponification it yields a small quantity of volatile acid (Chevreul), and besides oleic acid, a liquid acid of lower atomic weight, whose baryta-salt dissolves more readily in ether, and when not perfectly pure, contains 45·62 p. c. C., 6·44 H., 14·56 O., and 33·38 BaO. (Heintz, *Pogg.* 89, 582). — *Beef-marrow* is bluish-white, melts at 45° (Berzelius), at 45·5° (Eylerts), and solidifies on cooling (at 35°, according to Eylerts) to a granular mass. It dissolves partially in boiling alcohol, the solution depositing white flocks on cooling; in ether also it dissolves with difficulty (Berzelius, *N. Gehl.* 2, 292). Contains the glycerides of palmitic, oleic, and medullic acids, the last ($C^{42}H^{42}O^{4}$) to the amount of 10 p. c. It does not contain stearic acid (Eylerts, *Pharm. Viertelj.* 9, 330; *N. Br. Arch.* 104, 129). — The oil called *Neat's foot oil* (*Klauenfett*), which runs at a gentle heat from the fresh feet of oxen (or of sheep) is pale yellow, destitute of taste and odour, and deposits a small quantity of tallow at low temperatures. It thickens but slowly, and does not turn rancid. With alcoholic ammonia it forms an amide, melting at 85° (Carlet). It is decolorised by chlorine, whereas other animal oils are blackened thereby (Chateau). See also Chateau on the adulterations of beef-suet (*Mulh. Soc. Bull.* 32, 365), beef-marrow (32. 405), and neat's foot-oil (32, 268), and the mode of distinguishing them.

39. *Palm-oil* or *Palm-butter* (*Handbuch* viii. *Phytochem.* 83). — Fresh palm-oil is reddish-yellow, of buttery consistence, has an aromatic odour, melts at 27°, and is then resolved, to the amount of about one-half, into acids and glycerin. The older the oil the higher the melting point, and the greater the proportion of free acids, so that in oil melting at 31°, the free acids amount to one-half, and in oil melting at 36°, to four-fifths of the whole (Pelouze & Boudet). Melts at 37° (Stenhouse). The melting point varies between 24·8° and 35·1°; the upper layers of old oil, which have been exposed to the air, melt at 42·2°, the lower at 36·5° (Pohl, *Wien. Akad. Ber.* 12, 480; *Lieb. Kopp's Jahresber.* 1854, 462). Palm-oil is perfectly bleached by exposure to the sun for a few days (Grassmann, *Repert,* 32, 55). By steam heated to 160°, it is bleached in two hours, and decomposed, with separation of fatty acids melting at 54° (Scharling, *J. pr. Chem.* 50, 376). — On the bleaching of palm-oil, see also Stenhouse (*Ann. Pharm.* 36, 50), Payen (*N. Ann. Chim. Phys.* 2, 53), Michaelis (*Pogg.* 27, 632). It gives off acid vapours when heated to 140° and above, and is bleached by heating it to 246° (even without access of light and air), and then pouring it into water. At 300° it boils, giving off the odour of acrolein, and yielding a distillate of fatty acids (Pohl). It dissolves in oil of vitriol, and deposits palmitic acid on standing (Frémy). It dissolves slowly and incompletely in cold alcohol, but mixes in all proportions with ether. Dissolves in oil of turpentine and oil of almonds, with separation of flocculent matters (Guibourt, *J. Chim. méd.* 1, 177; Henry,

J. Pharm. 51, 241). — Contains olein, terpalmitin (margarin, according to Pelouze & Boudet), together with free oleic acid, palmitic acid, and glycerin, also a peculiar ferment, which induces the decomposition of the glycerides (Pelouze & Boudet). See *Palmitic acid* (p 352), *Terpalmitin* (p 33), and *Palmitonic acid* (p 366).

40. *Para* or *Brazil-nut oil.* — From the nuts of *Bertholettia excelsa* (*Handbuch* viii. *Phytochem* 31), which yield 50 per cent. of oils. Pale yellow, inodorous, solidifying completely to a tallowy mass at 0° (Caldwell); remains semi-solid at 10° (Dureau). Does not dry up. It is solidified by nitric acid; dissolves slightly in cold, easily in boiling alcohol, and in all proportions in ether (Dureau, *N. J. Pharm.* 6, 132). Contains stearin, palmitin, and olein (Caldwell, *Ann. Pharm.* 98, 120).

41. *Pheasant's fat.* — Yellow, inodorous, greasy at common temperatures, but acquires the hardness of beef-suet at 9°. Perfectly fluid at 43°. Yields a hard, white, scentless soap (Joss).

42. *Pichurim-fat.* — From *Fabæ pichurim majores.* The fat extracted by cold alcohol is dark brown, buttery, non-crystalline; has the odour of the beans, and an acid reaction. It yields acrolein by distillation. When boiled with water, it gives off a volatile oil, and pichurim camphor (xv. 50); the residue is saponifiable, and appears to contain laurostearin. From the beans previously exhausted with cold alcohol, laurostearin (xv. 50) may be extracted by the use of boiling alcohol, followed by hot-pressing (Sthamer, *Ann Pharm.* 53, 390). — On the volatile oil of pichurim-beans, see A. Muller (*J. pr. Chem.* 58, 463).

43. *Fat of Pistacia Lentiscus* (*Handbuch* viii. *Phytochem* 18) — Obtained by comminuting and boiling the berries. Dark green; melts between 32° and 34°; may be separated by partial solidification and decantation of the fluid portion, into a white crystalline fat melting at 34° or 35°, and a dark green fat which remains liquid at 0° (Leprieur, *N. J. Pharm.* 37, 251; *Kopp's Jahresber.* 1860, 323).

44. *Fats of Plant-lice.* — From *Aphis rosæ* or *A. Sambuci.* — Extracted by boiling alcohol and purified by recrystallisation, whereupon it separates as a gelatinous mass, having a silky lustre. — Melts between 27° and 30° to a yellowish brown mass, solidifying but slowly. Tasteless, inodorous, neutral. Volatilises in a glass tube, giving off vapours which redden litmus, and leaving only a trace of charcoal. — With hot concentrated nitric acid, it forms a paste, then melts, gives off nitrous gas, and is converted into a white substance, similar to that which may be obtained by the action of sulphuric acid, and partially soluble in cold potash-ley. — It dissolves in cold oil of vitriol, forming a solution, which is colourless at first, but becomes rose-coloured in 12 or 16 hours, darker red in 24 hours, and deposits a jelly; water destroys the colour, and precipitates a white mass, which reddens litmus, is less fusible than the original fat, and crystallises in needles on cooling. The acid filtered from this deposit contains organic matter in solution. — The fat is soluble in alcohol, more freely in ether, and crystallises from the former in needles, from the latter in granules (Barruel, *J. Chim. méd.* 7, 486).

45. *Potato-fat.* — Fresh potatoes contain on the average 0·73 p. c. fat extractable by ethers, about half that quantity, but of different con-

stitution, existing in the peel. — The juice of bruised potatoes, from which the starch has settled down. is heated to boiling, whereupon albumin and fat separate out, and the latter is extracted by ether. Peeled potatoes thus treated, yield a comparatively light-coloured solid-fat; unpeeled potatoes a dark liquid fat. By evaporating the ethereal solution, there are obtained from peeled potatoes: *a.* White, slender, stellate needles, which turn brown at 270°, without melting, are not saponifiable, resemble suberin, and contain, on the average, 71·34 p. c. C., 10·8 H.. and 15·58 O. These, according to Eichhorn, may be represented by the formula $C^{36}H^{30}O^7$.

b. The mother-liquor leaves when evaporated a yellow buttery fat, consisting of a mixture of fatty acids, free from glycerides, and easily soluble in aqueous carbonate of soda. This fat melts at 42·5°, contains between 70·5 and 75·8 p. c. C., 10·7 and 11·7 H., and alters quickly in contact with the air. By saponification, decomposition with hydrochloric acid, and solution in aqueous alcohol, it yields crystals of fatty acids, melting at 52°. On dissolving these in alcohol, and mixing the solution with a small quantity of neutral acetate of lead, thin laminæ crystallise on cooling, from which an acid melting at 50° may be separated. The mother-liquor mixed with a large quantity of neutral acetate of lead, yields the lead-salt¹ of an acid melting at 58°; but the quantity obtained was too small for further investigation. The acid melting at 50°, Eichhorn's *Solanostearic acid*, is difficult to crystallise; its silver-salt contains 51·05 p. c., C., 8·86 H., 6·98 O., and 33·11 AgO., agreeing approximately with the formula $C^{30}H^{29}AgO^4$. This, or a similarly constituted acid (73·79 p. c. C., 12·52 H., and 74·63 C., 13·09 H.) is likewise obtained by the distillation of potato-fat. It is, according to Heintz, a mixture of palmitic and myristic acids.

c. Unpeeled potatoes, cut in slices, dried at 100°, pulverised and exhausted with alcohol, yield, after evaporation of the alcohol, an extract, from which ether dissolves a brown syrupy fat. On dissolving this in potash-ley, separating it out again with acid, and mixing it in alcoholic solution with ammonia and chloride of barium, baryta-salts of the above-mentioned solid fatty acids are precipitated. while Eichhorn's *Solanoleic acid* remains dissolved, and may be obtained by evaporation as a viscid baryta-salt, from which, alcoholic hydrochloric acid separates the acid, still coloured brown. This solanoleic acid is not converted into elaïdic acid by nitrous acid, and is but partially, or not at all, precipitated from its alcoholic solution by alcoholic neutral acetate of lead. It occurs also, though in smaller quantity, in the fat of peeled potatoes (Eichhorn, *Pogg.* 87, 227).

Sheep-fat see *Mutton-fat* (p. 394).

46. *Fat* or *wax of Shellac.*—Obtained from true and false shellac by solution in boiling alcohol and cooling. — White, dries slowly; friable; melts at 60°. When heated, it chars and emits a disagreeable odour, like that of a recently extinguished tallow candle. Makes grease-spots on paper. It is not coloured by cold oil of vitriol, the acid acquiring a reddish colour only after 18 hours. With boiling potash-ley, it forms a soap, which is insoluble in the caustic solution, is resolved into a frothy liquid by immersion in warm water, and is reprecipitated by alcohol. The precipitate formed by alcohol dissolves partially in water, and the solution is rendered turbid by acids. — The fat is slightly soluble in cold ether, rock-oil, oil of turpentine, and oil

of almonds, the latter solution solidifying to an unctuous mass on cooling (Nees v. Esenbeck & Marquart, *Ann. Pharm.* 13, 288.)

Spermaceti, see page 347.

47. *Turtle-fat.* — Contains the glycerides of oleic and margaric acids, with only a small quantity of volatile acids (Ch. Link, *Lieb. Kopp's Jahresb.* 1850, 403).

48. *Tallow of Vateria indica.* — Obtained by boiling the fruit with water. It is white or yellow, greasy and waxy to the touch; spherico-radiate on the fractured surface; tasteless; has a faint agreeable odour; sp. gr. 0·926 at 15°, 0·8965 at 36·4°, at which temperature it melts. By pressure between bibulous paper, it yields a very small quantity of oil. It is coloured dirty green by chlorine gas, and sapo-nified by alkalis. From the pulverised tallow, cold alcohol of sp. gr. 0·82 extracts 2 p. c. of fixed oil, together with colouring and odori-ferous matter; boiling alcohol likewise extracts a small quantity of tallow, which melts at 37°, and crystallises on cooling (Babington, *Quart. J. of Sc.* 19, 177).

49. *Fats of Wool.* — From greasy wool, previously drenched with water, alcohol extracts a solid and a liquid fat, called respectively *Stearerin* and *Elaierin;* the quantity amounts to 20·8 p. c. of the washed and dried wool; but wool washed on the large scale, with addition of alkaline liquids, yields a much smaller quantity. These two fats may be separated by their different degrees of solubility in alcohol. — A. *Stearerin* melts at 60°, is neutral, apparently free from nitrogen and sulphur. It does not form an emulsion when boiled with water; but by boiling it with 2 pts. hydrate of potash and with water, an emulsion is formed without saponification of the fat. It dissolves in 1000 pts. alcohol of sp. gr. 0·805 at 15°. — B. *Elaierin:* Melts at 15°. Neutral. Forms an emulsion when boiled with water, and is saponified by hydrate of potash. Dissolves in 143 pts. alcohol of sp. 0·805 at 15°. — When the two fats are heated with water and hydrate of potash for 125 hours in contact with the air, no solution is obtained, but the fats appear to be completely altered. On mixing the alkaline liquid with phosphoric acid, and separating the acid solution from the precipitated fat, the latter is found to consist of one or two neutral substances, and two acids of different melting point, the alkaline salts of which resemble resin-soaps. The acid solution yields by distillation, a volatile acid, having the odour of delphinic (valerianic) acid (Chevreul, *Rev. scient.* 1, 368. — *Compt. rend.* 14, 783; *J. pr. Chem.* 27, 57).

Oxygen-nucleus C³²H³⁰O².

Jalapinolic Acid.

$$C^{32}H^{30}O^6 = C^{32}H^{30}O^2,O^4.$$
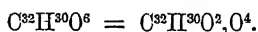
W. Mayer.   *Ann. Pharm.* 95, 149.
Keller.   *Ann. Pharm.* 104, 63; further with corrected data, 109 209.
Spirgatis.   *Ann. Pharm.* 116, 304.

Scammonolic acid.

Formation. 1. By treating jalapinol with caustic alkalis, or with baryta (Mayer). — 2. By the action of melting hydrate of potash on jalapin, or jalapic acid (Mayer). Jalapin and jalapic acid prepared from scammony, are resolved by mineral acids into jalapinolic acid and sugar (Spirgatis). Comp. Keller's statements (p. 408).

Preparation. 1. Jalapin is added gradually and by small portions to hydrate of soda melted with $\frac{1}{8}$ water (the mass then frothing up violently, giving off hydrogen, and turning brown); the mixture is heated and stirred as long as hydrogen continues to escape; the crumbling light-yellow mass is dissolved in water after cooling; and the greater part of the alkali is neutralised with acid. The jalapinolate of soda, which separates after some hours, is collected, washed, and decomposed by fusion with hot acidulated water; the separated acid is again repeatedly melted with pure water, then dissolved in alcohol and treated with animal charcoal; the somewhat concentrated filtrate is mixed with a large quantity of warm water; and the solid acid which separates on cooling is collected (Mayer). From the mother-liquor filtered from the jalapinolate of soda, excess of acid still separates a small quantity of impure jalapinolic acid (Mayer). — 2. The hot aqueous solution of jalapic acid (from scammony) is digested in the water-bath for a fortnight with dilute sulphuric acid; and the tallowy mass which separates on cooling, is freed from sulphuric acid by washing with hot water, and crystallised from ether, with help of animal charcoal (Spirgatis). — 3. Jalapin from scammony is added to boiling baryta-water; the liquid is heated till the whole is dissolved, and a sample of the filtrate is not rendered turbid, either by water or by hydrochloric acid; and the solution, after filtration, is mixed with one-third of its volume of fuming hydrochloric acid. The liquid becomes turbid in about 20 hours, and solidifies in the course of 10 days to a thick pulp, which is collected, washed with cold water, re-melted with hot water, and recrystallised 4 or 5 times from aqueous alcohol.

Properties. White tufts of needles, appearing under a magnifying power of 300, as thin 4-sided prisms. Melts at 64° or 64·5° (60° to 61°, according to Keller), and solidifies at 61·5° or 62° (Meyer), at 50° (Spirgatis), to a white, radio-crystalline, hard and brittle mass. — Makes grease-spots on paper. Lighter than water; inodorous; has an irritating taste and acid reaction (Mayer, Spirgatis).

at 100°.				Mayer. *mean.*		Spirgatis. *mean.*		Keller. *mean.*
32 C	....	192	... 71·11	.... .. 71·01	....	71·08	....	70·15
30 H	....	30	.... .. 11·11	.... .. 11·45	....	11·55	....	11·56
6 O	... .	48	... . 17·78	...... 17·54	.. ....	17·37	....	18·29
$C^{32}H^{30}O^6$	....	270	.. .... 100·00	.... 100·00	....	100·00	....	100·00

Keller gave other formulæ, finally $C^{30}H^{28}O^6$ or $C^{30}H^{30}O^6$.

Decompositions. Jalapinolic acid *heated* above its melting point, decomposes with intumescence, emitting a pungent odour which attacks the eyes and throat. — *Nitric acid* oxidises it to ipomæic acid (xiv. 493) and oxalic acid (Mayer, Spirgatis).

Combinations.   Insoluble in *water.*—Unites with *bases,* forming the jalapinolates.

Jalapinolate of Ammonia.—By dissolving jalapinol or jalapinolic acid in aqueous ammonia, an opalescent liquid is obtained, which gives off ammonia when evaporated, solidifies to a crystalline mass when concentrated to a certain point, but if completely evaporated, leaves an amorphous neutral jelly soluble in water.—The crystals are grouped like cauliflower-heads, and when strongly magnified, appear as long colourless needles.   After drying over lumps of potash-hydrate, they contain 4·25 p. c. NH⁴O, and are therefore C³²H²⁹O⁵,NH⁴O + C³²H³⁰O⁶ (calc. 4·66 p. c. NH⁴O) (Mayer).

Jalapinolate of Potash.—Dilute boiling potash-ley quickly dissolves jalapinol, and the solution solidifies on cooling to a crystalline pulp, which is to be washed, and then recrystallised from water or alcohol. Slender, white, silky needles, melting without decomposition when heated.   Neutral.—It forms an opalescent solution with water, even when free alkali is present.   Soluble in alcohol (Mayer).

Jalapinolate of Soda.—Slender dazzling-white tufts of needles which form a turbid solution with a small quantity of hot water, a clear neutral solution with a larger quantity, and are likewise soluble in alcohol.   Contains 10·08 p. c. soda.   (C³²H²⁹NaO⁶ = 10·62 p. c. NaO) (Spirgatis).

Jalapinolate of Baryta.—Obtained by precipitating jalapinolate of ammonia with chloride of barium, or by boiling jalapinol or alcoholic jalapinolic acid with baryta, the salt then crystallising out on cooling.—Microscopic, thin, white, lustreless needles, melting to a colourless liquid when heated.   Nearly insoluble in cold, sparingly soluble in boiling water,   more easily in boiling aqueous alcohol (Mayer, Spirgatis).

		at 120°.				Mayer. *mean.*		Spirgatis. *mean.*
32	C	192·0	....	56·88	....	56·50	....	56·71
29	H	29·0	....	8·59	....,	8·92	....	9·00
5	O	40·0	....	11·87	....	12·18	....	11·74
	BaO	76·5	... ...	22·66	...	22·40	....	22·55
C³²H²⁹BaO⁶		337·5	......	100·00	. .	100·00	...	100·00

Jalapinolate of ammonia precipitates aqueous *chloride of calcium.*

Jalapinolate of Lead.—Obtained by precipitating alcoholic jalapinolic acid mixed with a little ammonia, with neutral acetate of lead, and washing the white amorphous precipitate with dilute alcohol and water.   Sinters together to an opaque mass at 120°.   Sparingly soluble in water and alcohol.

				Mayer. *mean.*		Spirgatis.
C³²H²⁹O⁵	....	261	....	69·97		
PbO	.. . .	112	....	30·03	....	29·81	....	29·89
C³²H²⁹PbO⁶	....	373	....	100·00		

Jalapinolate of ammonia precipitates *iron-salts.*

Jalapinolate of Copper. a. *Basic.*—When a slightly alkaline aqueous solution of the ammonia-salt is precipitated with cupric acetate, and the precipitate is washed and dried at 100°, a dark blue-green, amorphous, very loose mass is obtained. which melts, without loss of water, to a dark green liquid, and solidifies to a translucent brittle mass. —Insoluble in water, nearly insoluble in alcohol. Contains at 100°, 18·75 p. c. cupric oxide, and is therefore $2C^{32}H^{29}CuO^6 + CuO,HO$ (calc. 18·24 p. c. CuO) (Mayer).

b. *Neutral.*—A hot aqueous solution of jalapinolate of soda forms a green-blue precipitate with hot aqueous cupric sulphate.—Light blue-green amorphous powder, which melts to a dark green liquid when heated (Spirgatis).

	at 100°.		Spirgatis. mean.
$C^{32}H^{29}O^5$	261	86·72	....
CuO	40	13·28	13·24
$C^{32}H^{29}CuO^6$	301	100·00	

Jalapinolate of Silver.—The alcoholic solution of the acid neutralised with ammonia is precipitated by a warm solution of nitrate of silver. —Flakes having a scarcely perceptible crystalline character (Keller).

				Keller. mean.
32	C	192	50·93	49·32
29	H	29	7·69	8·04
6	O	48	12·73	13·16
	Ag	108	28·65	29·48
$C^{32}H^{29}AgO^6$		377	100·00	100·00

Jalapinolic acid is soluble in *alcohol* and in *ether*.

Jalapinolate of Ethyl.

$$C^{36}H^{34}O^6 = C^4H^5O,C^{32}H^{29}O^5.$$
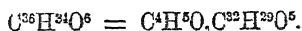
Spirgatis. *Ann. Pharm.* 116, 313.

Scammonolate of Ethyl. Jalapinolic or Scammonolic ether.

When hydrochloric acid gas is passed into a solution of jalapinolic acid in absolute alcohol, and the resulting liquid is mixed with water, a yellow oil separates, which must be washed, after solidification, with cold alcohol, dissolved in boiling alcohol, mixed with carbonate of soda, and after it has separated out on cooling, repeatedly precipitated from the alcoholic solution by water. It may also be obtained from scammony resin, by passing hydrochloric acid gas into the alcoholic solution (Spirgatis).

				Spirgatis.
				mean.
36 C	216	....	72·18	72·39
34 H	34	....	11·41	11·65
6 O	48	.... .	16·11	15·96

| C³²H²⁹O⁵,C⁴H⁵O | 298 | .. .. | 100·00 | 100 00 |

Jalapinol.

$$C^{32}H^{31}O^7 = C^{32}H^{30}O^6,HO ?$$
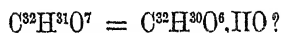
W. Mayer. *Ann. Pharm.* 95, 145.

Formation. Jalapin and jalapic acid are resolved by contact with mineral acids, slowly at ordinary, more quickly at elevated temperatures, into jalapinol and sugar. Jalapinol and sugar were also produced, in one insⴠⴠnce, when aqueous jalapic acid was left for 24 hours in contact with emulsion of almonds at 36° to 38°, whereas in a second experiment pure emulsin did not effect the decomposition, perhaps because the solution was too strongly heated.

Preparation.   From Jalapic acid. — A moderately concentrated aqueous solution of jalapic acid is mixed with half its bulk of fuming hydrochloric acid, and left to itself for 6 or 8 days, or till the clear mixture has solidified to a thick crystalline pulp; and the product, after being washed on a filter with cold water, is repeatedly melted under warm water, and purified by recrystallisation from alcohol, with help of animal charcoal.

Properties. White, cauliflower-like crystals, which melt at 62° or 62·5°, and solidify at 59·5° to a hard, brittle, crystalline mass. Makes grease-spots on paper. Inodorous; has an irritating taste, and weak acid reaction.

				Mayer.
	In vacuo or at 100°.			*mean.*
32 C	192	....	68·82	68·65
31 H	31	....	11·11	11·33
7 O	56	....	20·07	20·02

| C³²H³¹O⁷ | 279 | .... | 100·00 | 100·00 |

In contact with *caustic alkalis*, aqueous *ammonia*, or *baryta*, it is converted, with elimination of water, into a salt of jalapinolic acid:

$$C^{32}H^{31}O^7 + BaO,HO = C^{32}H^{29}BaO^6 + 3HO.$$
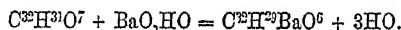
Jalapinol is soluble in *alcohol* and in *ether*.

Glucosides of Jalapinolic Acid.

Jalapin.

$$C^{68}H^{56}O^{32} = C^{32}H^{26}O^2,3C^{12}H^{10}O^{10}.$$
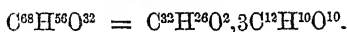
J. JOHNSTON. *Phil. Trans.* 1840, 342; *London Edinb. Phil. Mag.* 17, 183.

A. KAYSER. *Ann. Pharm.* 51, 101.

W. MAYER. *Ann. Pharm.* 95, 129; abstr. *J. pr. Chem.* 67; 267; *Pharm. Centr.* 1855, 797; *N. Ann. Chim. Phys.* 45, 494. — Preliminary notice: *Ann. Pharm.* 92, 115.

For jalapin from scammony-resin:

JOHNSTON. *Phil. Trans.* 1840, 340.

FR. KELLER. *Ann. Pharm.* 104, 63; further, with altered data: *Ann. Pharm.* 109, 209.

SPIRGATIS. *Münch. Akad. Bull.* 13, 106; abstr. *Instit.* 1858, 289; *Kopp's Jahresber.* 1858, 450; *N. Repert.* 3, 23, and (in detail) 7, 1. — In full: *Ann. Pharm.* 116, 289; thence in abstract, *Chem. Centr.* 1861, 116; *Kopp's Jahresber.* 1860, 490.

Kayser's *Pararhodeoretin.* — Occurs in the root-stock of *Ipomœa orizabensis* (*Handbuch.* VIII. *Phytochem.* 60), the jalap-stalks of commerce, and forms the principal portion (soluble in ether) of the jalap-resin prepared therefrom. — On the resin of tuberose jalap-root, see page 154; also on Buchner & Herberger's jalapin. — On the jalapin of Hume (*Mag. Pharm.* 7, 195), and of Meylink (*Repert.* 32, 443), see the places just cited, and Dulk (against Hume), *Berl. Jahrb.* 27, 1, 41.

The resin of jalap-stalks has been examined also by Hänle (*Repert.* 48, 365), and Planche (*J. Pharm.* 24, 169). According to Weppen (*N. Br. Arch.* 87, 153), the resin of *Convolvulus arvensis* is perhaps identical with jalapin, inasmuch as it assumes a fine purple-red colour with sulphuric acid, and is soluble in ether (contrary to the statement of Planche, *J. Pharm.* 13, 165, who found it insoluble in ether). — The same resin has been examined by Chevallier (*J. Pharm.* 9, 306). — The resin of *Convolvulus Soldanella* appears, according to Planche (*J. Pharm.* 13, 165), to be freely soluble in ether and alcohol, as also the portion of the tuberose jalap-roots which is soluble in ether, described at p. 159; both these resins are therefore, perhaps, jalapin.

Commercial scammony resin, from *Convolvulus Scammonia* (*Handbuch.* viii. *Phytochem.* 60), was described some years ago, by Bouillon-Lagrange & Vogel; also by Planche (*J. Pharm.* 13, 165; 18, 183). Cl. Marquart (*N. Br. Arch.* 7, 248; 10, 139) described the resin obtained from the root, and believed he had separated from it a vegetable base (*Convolvuline*). — Johnston recognised the similarity between scammony-resin and the resin of jalap-stalks; Spirgatis showed that *scammonin*, the chief constituent of the former, is either identical with jalapin, or differs from it only in so far that, when decomposed by acids, it at once yields scammonolic (jalapinolic) acid, whereas jalapin, according to Meyer, when treated in a similar manner, yields at first jalapinol (comp. xv. 345). These statements are, perhaps, better founded than the contrary statements of Keller & Kosmann (pp. 407, 408).

According to Planche, the resin of *Convolvulus sepium*, and according to Boutron-Charlard, that of *Conv. Turpethum* (*J. Pharm.* 8,

131), are not soluble in ether, and may thus be distinguished from jalapin.

In what follows, the statements of Kayser and Mayer relate to jalapin from jalap-stalks, those of Keller & Spirgatis, to that from scammony.

Preparation. A. From commercial *Resina Jalappae ex stipitibus.* To a solution of the resin in a large quantity of alcohol, water is added until it becomes slightly turbid; the whole is repeatedly boiled with animal charcoal; and the still coloured filtrate is precipitated by neutral acetate of lead and a little ammonia, which produces a slight greenish brown precipitate. The liquid is filtered, and the filtrate freed from lead by passing hydrosulphuric acid through it, then heating and filtering; the alcohol is again distilled off; and the resinous residue is repeatedly kneaded in boiling water, then dissolved in ether, from which it may be recovered by evaporation (Mayer). Or the alcoholic resin, after treatment with animal charcoal, is boiled for a long time with freshly precipitated hydrated oxide of lead; the lead is separated from the filtrate by hydrosulphuric acid; and the resin is three times separated by water from the alcoholic solution, then well boiled in water, and dissolved in ether (Mayer). Kayser exhausts the root with alcohol; evaporates the tincture; washes the resinous residue with hot water; dissolves it in alcohol, and treats the solution with animal charcoal; distils off the alcohol; boils the residue again with water; and dries it over a water-bath. — Johnston examined a resin obtained either by dissolving the commercial resin in ether and evaporating the solution; or by exhausting the ground root of commerce with hot alcohol, evaporating the brown tincture, and exhausting the residue with ether; or by exhausting chips of the root with cold alcohol, evaporating, boiling the residue in water, dissolving the resinous residue in ether, and evaporating the solution.

B. *From Scammony.* Coarsely powdered scammony is exhausted with cold alcohol (boiling, according to Keller); the tincture is diluted with water till it becomes turbid, then decolorised by animal charcoal, and filtered; and the greater part of the alcohol is distilled off. The residue mixed with water is heated in a water-bath, till the whole of the alcohol is driven off, after which the resin is treated for a long time (even for 4 weeks) in a water-bath, with frequently renewed hot water, and at last dried up. The residue may be dissolved in ether and recovered by evaporation (Spirgatis).

The jalapin (obtained according to A or B) still contains a small quantity of a volatile acid (valerianic acid, according to Keller) which cannot be completely removed, even by very long washing. It betrays itself by the smell which the jalapin emits when it is converted by bases into jalapic acid, and the resulting solution supersaturated with a mineral acid. Keller regards this acid, the bulk of which passes off in the water used in washing the jalapin, as an essential product of the decomposition of scammony, whereas Mayer and Spirgatis regard it as a mere contaminatio⁻

Properties. Colourless, amorphous resin, translucent when in thin _ tes; at 100° it becomes brittle, and may be rubbed down to a white powder. It softens at 123°, and melts at 150° to a transparent, colourless, or pale yellow syrup. It is tasteless and inodorous; in alcoholic solution it gives a scarcely perceptible acid reaction (Mayer, Spirgatis).

At 103°, or in vacuo.			Kayser.	Mayer.	Keller.	Spirgatis.
68 C	408	56·66	58·13	56·52	56·65	56·47
56 H	56	7·77	8·07	8·18	8·39	7·93
32 O	256	35·57	33·80	35·30	34·96	35·60
$C^{68}H^{56}O^{32}$	720	100·00	100·00	100·00	100·00	100·00

The analyses are given in mean numbers. Johnston found in the resin obtained from jalap-stalks, 55·76 to 56·65 p. c ; in scammony resin 54·06 to 55·32 p. c. carbon. — Keller gives the formula $C^{54}H^{46}O^{24}$.

Decompositions. 1. When *heated* above 127°, it gives off carbon and hydrogen in the form of a volatile compound, which contains less oxygen than the residual resin (Johnston). Jalapin which melts at 150°, becomes brown when further heated, and acquires a pungent empyreumatic odour (Spirgatis). — 2. When heated on platinum-foil, it takes fire, *burns* with a bright sooty flame and empyreumatic odour, and leaves charcoal.

3. It dissolves slowly in cold *oil of vitriol*, the solutions in five or ten minutes, acquiring a beautiful purple or maroon-red colour, then becoming brown, and finally black. On standing or after dilution, a brown resin or a brown tallowy body separates from the liquid, while sugar remains dissolved. The reaction is the same as in 4, but the resulting products undergo a further alteration (Kayser, Mayer, Spirgatis).

4. By heating with dilute mineral acids, jalapin (even that which has been dissolved in alkalis and thereby converted into jalapic acid) is decomposed into jalapinol and sugar (Mayer). When jalapin from scammony is treated in the same way, jalapinolic acid is obtained in place of jalapinol (Spirgatis). Formation of jalapinol :—

$$C^{68}C^{56}O^{32} + 11HO = C^{32}H^{31}O^7 + 3C^{12}H^{12}O^{12} \text{ (Mayer).}$$

Of jalapinolic acid :—

$$C^{68}H^{56}O^{32} + 10HO = C^{32}H^{30}O^6 + 3C^{12}H^{12}O^{12}.$$
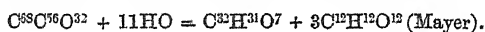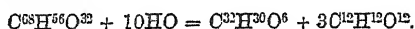
If pure jalapin (or pure jalapic acid) is used no other bodies are formed than those just mentioned (Mayer, Spirgatis).

According to Keller, when a solution (alkaline or alcoholic?) of scammonin is treated with oil of vitriol or hydrochloric acid gas and left to itself, three decomposition products result, and the formation of a fourth (formic acid or formic aldehyde) appears probable from the formulæ. The products of this decomposition are: *a.* a *neutral body*, $C^{28}H^{28}O^4$, further separable by alkalis into scammonolic acid (jalapinolic acid) and an alcohol $C^{26}H^{28}O^2$.—*b. Amylic aldehyde*, which passes over as valerianic acid, when scammony resin is boiled with potash-ley and then with dilute sulphuric acid. — *c.* A *carbo-hydrate*, which, however, is converted into sugar by simple boiling with dilute sulphuric acid. Keller gives the equation :

$$C^{76}H^{67}O^{35} = C^{28}H^{28}O^4 + C^{10}H^{10}O^2 + 3C^{12}H^9O^9 + C^2H^2O^2.$$
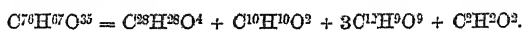
But according to Spirgatis, the neutral body *a* must be regarded as ethyl-scammonolic ether ; moreover, the valerianic acid is obtained only from impure scammonin.

Kosmann, who takes no account of the investigation of scammony resin by other chemists, obtains, by boiling scammony resin with dilute

sulphuric acid, sugar, and his *scammoneol*, as a soft, yellowish-white substance having a silky lustre and acid reaction, and separating from the hot alkaline solution on cooling.—He calculates, according to Johnston's analysis of scammony-resin, the formula $C^{64}H^{52}O^{32}$ for scammonin and so arrives at the equation of decomposition: $C^{64}H^{52}O^{32}$ + $10HO = 3C^{12}H^{12}O^{12} + C^{28}H^{26}O^6$ (Kosmann, *N. J. Pharm.* 38, 83).

5. When jalapin is dissolved in aqueous *caustic alkalis*, *ammonia*, or *baryta water*, or in boiling *alkaline carbonates*, water is assimilated and jalapic acid soluble in water is formed (Mayer, Spirgatis): $C^{68}H^{56}O^{32} + 3HO = C^{68}H^{59}O^{35}$. Even the purest jalapin, quite free from ash, yields traces of jalapinolic acid and a volatile acid, but no sugar (Mayer). When jalapin is melted with *hydrate of soda*, hydrogen is given off and jalapinolic and oxalic acids are formed (Mayer).

Keller, by boiling scammonin with alcoholic potash obtained dark flakes (on account of impurities in the scammonin; *Spirgatis*), and on subsequently adding water to the solution, the compound $C^{26}H^{28}O^2$ was precipitated in white flakes, while valerate of potash remained in solution. The body, $C^{26}H^{28}O^2$ regarded by Keller as an alcohol is likewise formed on boiling commercial jalapin (obtained from the resin of jalap-stalks) or scammony, with baryta-water or solution of potash; it evaporates with the water and separates in gelatinous flakes from the distillate. At 40° it melts to an oil, crystallises on cooling, and contains, on the average, 78 p. c. C., 14·12 H + 7·88 O. Keller regards this body as a product of the decomposition of scammonin (or more exactly of the neutral body $C^{28}H^{28}O^4$, p. 407); Spirgatis regards it as a mixture of resins, since the greater portion of it is obtained on distilling the impure resin with water.

6. By *nitric acid* jalapin is at first decomposed into jalapinol and sugar, and these products, when further subjected to the action of the nitric acid, are converted into ipomæic (xiv, 494) and oxalic acids (Mayer). A small quantity of nitric acid does not colour jalapin; but in presence of guaiac resin, a green colour is produced (Bull. Spirgatis).—7. When *sulphurous acid* is passed through an ammoniacal alcoholic solution of scammony resin, silvery shining plates are separated, containing perhaps an aldehyde in combination with bisulphite of ammonia (Keller).

Jalapin is but slightly soluble in *water*.—It dissolves very easily and without decomposition in *wood-spirit*, *alcohol*, *ether* and *chloroform*, and in warm *acetic acid*. It is soluble in *benzene* and *oil of turpentine* (Mayer), in *rock-oil* and *oil of turpentine* less freely than in ether and benzol (Spirgatis).

Jalapic Acid.

$$C^{68}H^{59}O^{35} = C^{32}H^{29}O^5,3C^{12}H^{10}O^{10}.$$
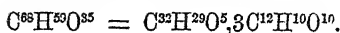
W. Mayer. *Ann. Pharm.* 95, 129.
Keller. *Ann. Pharm.* 104, 28.
Spirgatis. *Ann. Pharm.* 116, 297.

Scammoninic or *Scammonic acid.* — *Jalappinsaure, Scammoninsaure* or *Scam-*

monsaure.—Produced, with assimilation' of 3 at. water, by dissolving jalapin in aqueous solutions of the alkalis or alkaline earths.

Preparation.—Jalapin is heated with baryta-water to the boiling point, until the whole is dissolved, and acids no longer form a precipitate in the solution; the baryta is then removed by sulphuric acid; the excess of this acid by hydrated oxide of lead; and the dissolved lead by hydrosulphuric acid. The filtrate is boiled to remove the hydrosulphuric acid, and on evaporation deposits jalapic acid, which, in case it has become coloured. may be decolorised by treatment with animal charcoal, or by boiling it with a little hydrated oxide of lead and subsequently passing hydrosulphuric acid through the liquid. (Mayer, Spirgatis). The small quantity of volatile acid which accompanies it is driven off during the concentration of the liquid, and the jalapinolic acid which is also formed (about $\frac{1}{4}$ p. c.) separates from the aqueous jalapic acid when it has been boiled down to a syrup and left at rest.

Properties.—Translucent, amorphous, shining, yellowish, brittle mass, which does not soften below 100° and at about 120° melts to a turbid syrup. Very hygroscopic. It has no smell, but an irritating sweetish taste (Mayer), or a sourish irritating taste, with bitter aftertaste (Spirgatis). It has a strong acid reaction.

	at 100°.			Mayer. *mean.*		Spirgatis. *mean.*
68 C	108	. ....	54·62	... .	54·38	... . 54·59
59 H	59	....	7·89	... .	8·34	.... 8·16
35 O........	280	....	37·49	. ....	37·28	.... 37·25
$C^{68}H^{59}O^{35}$	747	.... ..	100·00	....	100·00	.... 100·00

Mayer examined jalapic acid prepared from jalap-stalks; Spirgatis, that from scammony. The former also divided jalapic acid into separate portions by fractional precipitation with ammoniacal sugar-of-lead, and found that the acid separated from these precipitates was similar in composition.

Decompositions.—1. Jalapic acid decomposes at about 130°; when heated on platinum foil, it *burns* with a bright sooty flame.—2. When a concentrated aqueous solution is stirred for a long time with fuming *hydrochloric acid*, it splits up into jalapinol and sugar (Mayer); the jalapic acid obtained from scammony forms jalapinolic acid instead of jalapinol (Spirgatis) (see p. 105). The same decomposition appears to be caused by emulsin (Mayer). Mayer obtained alphajalapic acid by boiling jalapic acid with dilute acids (p. 411).—3. By *nitric acid* it is converted into ipomœic (xiv, 494) and oxalic acids.—4. When melted with *hydrate of soda*, it gives off hydrogen and forms jalapinolic and oxalic acids (Mayer, Spirgatis).

Combinations.—Jalapic acid is very soluble in *water.*—It unites with bases, forming three classes of *salts*, in which 1, 2, and 3. at. water are displaced by the same number of atoms of metallic oxide; mixtures of these different salts are however very apt to form. It displaces carbonic acid from the carbonates of the alkalis and alkaline earths. Even when neutralised with an alkali, it gives no precipitate with any metallic salt, except basic acetate of lead. The jalapates are amorphous.

Jalapate of Baryta. — A. *Terbarytic.* — Jalapin is boiled for four or six hours with 2 pts. hydrate of baryta and 4 pts. water (or it is mixed with an equal weight of hydrate of baryta, melted for half an hour in an air-bath, and then heated with water); and carbonic acid is passed through the boiling solution, which is then filtered and evaporated down; and the residue is dried at 100° in a current of air. — It is an amorphous, slightly coloured mass, having a slightly irritating, bitter-sweet taste.   Melts at 100°, and decomposes with intumescence when strongly heated.   Neutral.   It is soluble in water and alcohol, and is not decomposed by carbonic acid (Mayer, Spirgatis).   Mayer once obtained a salt with 25·65 p. c. baryta, containing therefore more than 3 at.; it was neutral, soluble in water, and not decomposible by carbonic acid.   By boiling jalapin with baryta-water for a shorter or for too long a time, or by leaving the mixture to itself for some time, salts are formed which contain varying proportions of baryta (from 11·66 to 22·28 p. c.), and are converted into the terbarytic salt by long boiling with excess of baryta (Mayer).

		at 100°.				Mayer. mean.		Spirgatis. mean.
68	C	408		42·97		42·08		42·26
56	H	56		5·88		5·99		6·02
32	O	256		26·98		27·78		27·50
3	BaO	229·5		24·17		24·15		24·22
$C^{68}H^{56}Ba^3O^{35}$		949·5		100·00		100·00		100·00

B. *Monobarytic.* — By mixing aqueous jalapic acid with a slight excess of baryta-water, passing carbonic acid through the liquid, then warming and evaporating the filtrate (Mayer).   Resembles the terbarytic salt.

		at 100°.				Mayer.
68	C	408		50·09		49·74
58	H	58		7·12		7·63
34	O	272		33·40		33·04
	BaO	76·5		9·39		9·59
$C^{68}H^{58}BaO^{35}$		814·5		100·00		100·00

Jalapate of Lead. — Recently precipitated hydrated oxide of lead dissolves in boiling aqueous jalapic acid, forming an amorphous, easily soluble salt.   When the aqueous acid is boiled for a long time with excess of hydrated oxide of lead, a gummy, tumefied, basic salt is formed, which is insoluble in water, and very sparingly soluble in alcohol. — The aqueous acid gives no precipitate with neutral acetate of lead, but copious white flakes with the basic acetate (Mayer, Spirgatis).   Ammoniacal acetate of lead or the basic acetate throws down from the aqueous acid, a flocculent precipitate, which may be purified by repeated solution in acetic acid, precipitation with ammonia, and washing.   After being dried over oil of vitriol, it does not lose weight at 130° (Keller).

						Keller.
68	C	408		38·63		34·55
56	H	56		5·30		5·23
32	O	256		24·24		26·86
3	PbO	336		31·83		33·36
$C^{68}H^{56}Pb^3O^{35}$		1056		100·00		100·00

Keller gives the formula $^T C^{76} H^{64} O^{13}, 4PbO$; but he seems to have examined the terplumbic salt with excess of lead-ox de.

Jalapic acid is easily soluble in *alcohol*, less easily in *ether*.

Alphajalapic Acid.

$$C^{56}H^{50}O^{26} = C^{32}H^{29}O^5, HO, 2C^{12}H^{10}O^{10}.$$
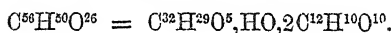
W. Mayer. *Ann. Pharm.* 95, 155.

Not named by Mayer.

When dilute aqueous jalapic acid is boiled for not too long a time with hydrochloric or dilute sulphuric acid, one part of the jalapic acid is completely converted into jalapinol and sugar, another smaller part into alphajalapic acid, which, on cooling, separates out with the jalapinol as a soft, brown, semi-crystalline mass. By boiling this mass with baryta-water, removing the jalapinolate of baryta which separates on cooling, and concentrating the mother-liquor, white silky needles of alphajalapic acid are obtained, while jalapinate of baryta remains in solution. — The needles are purified by recrystallisation from water; then dissolved in boiling water, and decomposed by acetic acid; and the alphajalapic acid, which crystallises out on cooling, is collected and purified by washing, recrystallising from water, acidulation with acetic acid, solution in alcohol, and precipitation with hot water.

Properties. White, flexible needles, exhibiting a silky lustre under water, melting below 8° to a pale yellow thin oil, and forming a crystalline solid on cooling. It has no smell, but an irritating taste, with sweetish after-taste. Feebly acid.

		Over chloride of calcium.				Mayer.
56 C	....	336	....	56·56	....	56 44
50 H	....	50	....	8·41	....	8 79
26 O	....	208	....	35·03	....	34·77
$C^{56}H^{50}O^{26}$	....	594	....	100 00	....	100·00

Decompositions. When the baryta-salt (or the acid itself) is *heated*, it is decomposed, with frothing, and gives off a brown acid oil, which solidifies on cooling, partly in the crystalline form. — When treated with *dilute acids*, or boiled with *nitric acid*, or melted with *hydrate of potash*, it exhibits the same reactions as jalapic acid. In these reactions, only 2 at. sugar are formed to 1 at. jalapinol, whereas jalapic acid yields 3 at. sugar :

$$C^{56}H^{50}O^{26} + 5HO = C^{32}H^{31}O^7 + 2C^{12}H^{12}O^{12}.$$
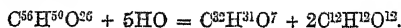
Alphajalapic acid dissolves sparingly in cold, more freely in boiling *water*.

Alphajalapate of Baryta.—*For the preparation see above.*—White, glittering, brittle, crystalline needles, having a sweetish irritating taste, and

melting easily to a thin oil without loss of water. — Soluble in water, especially in hot water, and in alcohol.

		at 100°.				Mayer.
56	C	336	....	50·79	....	50·56
49	H	49	....	7·40	....	7·46
25	O	200	....	30·25	....	30·32
	BaO	76·5	....	11·56	....	11·66
	$C^{56}H^{49}BaO^{26}$	661·5	....	100·00	....	100·00

Alphajalapic acid is very soluble in *alcohol* and in *ether*.

Oxygen-nucleus $C^{32}H^{24}O^{8}$.

Choloïdanic Acid.

$$C^{32}H^{24}O^{14} = C^{32}H^{24}O^{8},O^{6}.$$
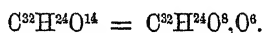
THEYER & SCHLOSSER. *Ann. Pharm.* 50, 243.
REDTENBACHER. *Ann. Pharm.* 57, 145.

Formation. Together with cholesteric acid (xiii, 157) and other products, on boiling choloïdic acid (Redtenbacher), or bile (Theyer & Schlosser) with nitric acid.

Preparation. Concentrated nitric acid is poured upon choloïdic acid to the extent of 4 or 5 times its bulk, and when the first violent action is over, the whole is heated in a retort connected with a condenser, the distillate being returned, and more nitric acid added when necessary, as long as red fumes are given off; the contents of the retort are then diluted with water, and boiled, so as to drive off the volatile acids. When the residue cools, choloïdanic acid separates from it, floating on the surface as a soft crystalline scum, which may be removed from the yellow-brown mother-liquor by filtration through pounded glass; it is rinsed in a little water, and dissolved in boiling water, for which purpose a large quantity is necessary, or repeated boiling, on account of the sparing solubility of the acid. Should the crystals which shoot out on cooling, be yellowish, they must be purified by recrystallisation. — If the boiling in nitric acid has not been continued long enough, a resin is obtained instead of choloïdanic acid, which may, however, be converted into that acid by boiling in nitric acid (Redtenbacher). — Theyer & Schlosser, by heating bile with concentrated nitric acid, obtained, with considerable frothing, a solution which, on cooling, deposited a granular crystalline powder. This was collected and washed, and obtained, by solution in hot alcohol and cooling, in small needles, which, for further purification, were dissolved in aqueous ammonia, and precipitated from the filtrate by sulphuric acid.

Properties. Long hair-like prisms, exhibiting a silky lustre under water, but presenting, when dry, the aspect of a very spongy film, like

asbestos. From alcohol it is obtained in small granules (Redtenbacher). It is precipitated from its ammonia-salt by sulphuric acid, as a white, tasteless, powder (Theyer & Schlosser). Has an acid reaction. Does not lose weight at 100°.

			Theyer & Schlosser. mean.		Redtenbacher. mean.
32 C	192	.... 58·54	... . 58·83	....	58·18
24 H	24	.... 7·31	... . 7·76	....	7·17
14 O	112	... . 34·15	... . 33·41	....	31·35
$C^{32}H^{24}O^{14}$	328	... ... 100·00	.... 100·00	... .	100·00

Redtenbacher's formula is the half of this, but is here doubled on account of the uneven number of oxygen-atoms.

The acid when *heated*, melts, chars, and gives off an irritating acid vapour. — When kindled, it *burns* with a sooty flame (Redtenbacher). It is nearly insoluble in cold, and but slightly in boiling *water*. It dissolves unchanged in warm *nitric* and *hydrochloric acids* (Redtenbacher).

The *alkaline choloïdanates* are soluble and uncrystallisable. With solutions of the *metallic salts*, they give flocculent precipitates, which are decomposed by washing with water. Redtenbacher found the atomic weight of the hypothetical anhydrous acid (regarded as mono-basic) to be 86 in the lead-salt, prepared by precipitating neutral acetate of lead with choloïdanate of ammonia, and washing with hot water; in the silver-salt, he found it to be 129 or 107, according to the method of washing.

Silver-salt. — Prepared from the neutral ammonia-salt and nitrate of silver (Theyer & Schlosser).

			at 100°.		Theyer & Schlosser.
32 C	....	192	....	29·18	.... 29·59
22 H	....	22	....	3·34	.... 3·55
15 O	..,............	120	....	18·24	.... 17·84
3 Ag	....	324	....	49·24	.... 49·02
$C^{32}H^{22}Ag^2O^{14},AgO$?		658	....	100 00	... ... 100·00

Choloïdanic acid dissolves easily in *alcohol* (Redtenbacher).

COMPOUNDS CONTAINING 34 AT. CARBON.

Primary Nucleus $C^{34}H^{24}$; *Oxyazo-nucleus* $C^{34}NH^{17}O^6$.

Morphine.

$$C^{34}NH^{19}O^6 = C^{34}NH^{17}O^6,H^2.$$
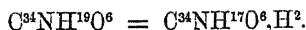
SERTÜRNER. *A. Tr.* 14, 1, 47; — 20, 1, 99; — *Gilb.* 55, 61; 57, 192; 59, 50.
SEGUIN. *Ann. Chim.* 92, 225; *N. Tr.* 1, 2, 117.

ROBIQUET.   *Ann. Chim. Phys.* 5, 275; *Gilb.* 57, 163; *Repert.* 4, 67.—
    J. Pharm. 19, 63; *J. Chim. méd.* 9, 71; *Ann. Chim. Phys.* 51, 232;
    Ann. Pharm. 5, 87; *Schw.* 67, 317; abstr. *Pogg.* 27, 646; *J. Pharm.*
    25, 82.
GÖBEL.   *Repert.* 11, 83.
PELLETIER & CAVENTOU.   *Ann. Chim. Phys.* 12, 122.
PFENDLER.   *Chem. Abhandl. uber das Opium.   Wien.* 1823.
ROBINET.   *J. Pharm.* 13, 24.—*J. Chim. méd.* 1, 357, 461 and 533;
    2, 101.
DUFLOS.   *N. Tr.* 10, 1, 3.—*Schw.* 61, 105.
MERCK.   *Mag. Pharm.* 13, 142; 15, 147.— *N. Tr.* 20, 1, 134.—*Ann.
    Pharm.* 18, 79; 21, 202; 24, 46.
GEIGER.   *Mag. Pharm.* 17, 218.
DUMAS & PELLETIER.   *Ann. Chim. Phys.* 24, 183.
PELLETIER.   *Ann. Chim. Phys.* 50, 240; *J. Pharm.* 18, 597; *Ann.
    Pharm.* 5, 150; *N. Tr.* 26, 1, 242; abstr. *Pogg.* 27, 639.—*J.
    Pharm.* 21, 557; *N. Br. Arch.* 5, 158; *Ann. Pharm.* 16, 27. —*Ann.
    Chim. Phys.* 63, 185; *Ann. Pharm.* 22, 120.—*J. Pharm.* 24, 164; *J.
    pr. Chem.* 14, 180; *Ann. Pharm.* 29, 56.
LIEBIG.   *Pogg.* 21, 16; —*Ann. Pharm.* 26, 42; *Ann. Chim. Phys.* 47,
    165.
REGNAULT.   *Ann. Pharm.* 26, 23; *Ann. Chim. Phys.* 68, 131.
RIEGEL.   *Jahrb. pr. Pharm.* 11, 103.— *N. Br. Arch.* 58, 285.
LAURENT.   *N. Ann. Chim. Phys.* 19, 361; *Ann. Pharm.* 62, 97; *J. pr.
    Chem.* 40, 402.
LEFORT.   *N. J. Pharm.* 40, 97; *Pharm. Viertelj.* 11, 243; abstr. *Anal.
    Zeitschr.* 1. 134.
GUIBOURT.   *N. J. Pharm.* 41, 1, 97 and 177; *Pharm. Viertelj.* 11, 489.

Morphia, Morphium. — Discovered by Serturner, and, as it is asserted, also by
Seguin in 1804.   His memoir, which was submitted to the Institute in 1804, was
nevertheless not printed till 1811.   See vii, 151.—For the controversy on the priority
of the discovery (*Gilb.* 65, 383; abstr. *J. Pharm.* 16, 179).
    On Pelletier's *nitrogenous hard resin, fat and caoutchouc* from opium, see *Ann.
Chim. Phys.* 50, 275; on Serturner's *Oxymorphium,* see *Ann. Pharm.* 29, 222.   The last
is a resinous extract, which is obtained by precipitating the aqueous infusion of
opium with ammonia, evaporating the filtrate, separating from the crystals, and
exhausting with alcohol, and remains as a residue on the evaporation of the alcohol.   An
acid called *thebolactic acid,* obtained from opium, was exhibited, together with its
copper- and morphine-salts, at the London Exhibition of 1862, nothing however being
known respecting them (*N. Repert.* 11, 519).   ¶ Thebolactic acid was obtained from
opium, and exhibited by T. & H. Smith, of Edinburgh.   It exists in Turkey opium
to the amount of about 2 per cent., and is separated by the insolubility of its lime-
salt.   It has the same composition as lactic acid, and is regarded by Stenhouse as
identical therewith; but some of its salts, especially the copper and morphine salts,
are said by the discoverers to differ in character from the corresponding lactates.
The ferric salts of the two acids are likewise said to differ in their reaction with
ammonia (T. & H. Smith.   *Epistolary communication*).¶
    Various constituents of opium, whose formulæ are unknown, are described in the
Appendix to Morphine.

Sources.   In opium, the juice of the white, black, or purple poppy,
obtained from incisions made in the capsules, and thickened by ex-
posure to the air; it occurs wholly or partly as a salt of meconic acid.
According to Guibourt, there are six kinds of opium to be distinguished.
a. *Anatolic* (so called *Smyrna*) *Opium.*   This, when dry, contains from
12 to 14 p. c. morphine (maxim. 21·46, minim. 11·7 p. c.), if it contains

less it may be regarded as adulterated (Guibourt). Merck found as much as 13·5 p. c. in fresh Smyrna opium, in other cases from 3 to 12 p. c. A. Petit, 3 to 17; Mulder found 3·3 to 12 p. c. in dry opium; most of the other statements vary between these numbers. — b. *Egyptian*. This contains, after drying, from 5·8 to 6·6 p. c.; in one case 12·2 p. c. was found (Guibourt); the undried substance contains from 6 to 7 p. c. (Merck). — c. *Persian*. Guibourt found in a dried sample 11·37 p. c. morphine, and 8·17 narcotine. Merck found at most 1 p. c. morphine. — d. *East Indian*. This, when dried, contains from 5·3 to 7·7 p. c. morphine (Guibourt). De Vry (*N. J. Pharm.* 17, 439) who found, in 21 sorts, from mere traces to almost 9·2 p. c. morphine, appears to have examined East Indian opium. Bengal opium, with 23 to 25 p. c. water, contained from 1·75 to 3·5 p. c. morphine (0·75 to 3·5 p. c. narcotine); that from Patna, with 13 p. c. water, contained 10·75 p. c. morphine, 6 p. c. narcotine; that from other Bengal districts, with 23 p. c. water, contained 4·5 p. c. morphine, and 4 p. c. narcotine (O'Shaughnessy). According to Eatwell (*Pharm. J. Trans.* 11, 269, 306, and 359; *Ann. Pharm.* 84, 385) freshly collected Bengal poppy-juice contains 0·555 p. c., and after deduction of the water, 1·4 p. c. morphine; the same juice dried at 96°, or evaporated slowly in open dishes, contains 2·49 and 2·61 p. c.; after deduction of the water, 3·1 and 2·9 p. c. morphia. Since, then, the fresh poppy-juice, even after the deduction of the water, contains less morphine than the dried juice, Eatwell is of opinion that the formation of morphine goes on after the collection of the juice. — e. *European*. In dry opium, which had been gathered at Erfurt in 1829 and 1830, from the blue poppy, Biltz found 16·6 and 20 p. c.; in that from the white poppy, 6·85 p. c. morphine. — French varieties, when dried, contain, on the average, 17·7 p. c. morphine (maxim. 22·9, minim. 14·8) (Guibourt). Opium collected at Brest, in 1852, contained 8·2 p. c. (Roux, *Compt. rend.* 40, 130); that from Amiens, in 1853, contained 14·75, and from the same place in 1854, 16 p. c. morphine (Descharmes & Benard, *Compt. rend.* 40, 34). — f. *Algerian*. Poppies cultivated in Algeria in 1844 and 1845, yielded opium, whose percentage of morphine differed according to the variety of the plants and the degree of maturity. Determinations by Aubergier, in which the morphine was decolorised by charcoal, and the percentages of morphine obtained were therefore perhaps too low (*Lieb. Kopp's Jahresber.* 1847-8, p. 6223) gave the following results for opium containing 7·6 p. c. water (*N. Ann. Chim. Phys.* 20, 303).

White poppies, 1844	1 crop	5–11 July	8·57 p. c.		
	2 „	17–20 „	1·52 „		
Red poppies	....	11–13 „	10 69 „		
White poppies......................	1 „	9 „	6·63 „		
	2 „	28 „	5·53 „		
		13 Aug.	3·27 „		
Red poppies...................... ..	1	21 July	10·87		
1845	2	26 „	10·69		
	3	16 Aug.	11·23		
Purple poppies...........	1 ..	29–30 July	17·83		
	2 „	21 Aug.	14·71		

Poppy-heads both ripe and unripe, contain morphine (Tilloy, *J. Chim. méd.* 3, 22. Winckler), also those of the *Papaver Rhoeas*. (Filhol, *N. J. Pharm.* 2, 150). It occurs in every separate part of the

white poppy (heads, leaves, branches, seeds), and at all stages of growth, but chiefly just before ripening (Meurein, *N. J. Pharm.* 23, 176, and 262). In dry ripe poppy-heads, Winckler found morphine and narcotine (*Repert.* 39, 468), subsequently (*Repert.* 59, 1) also narceïne; in the fresh, nearly ripe heads, not a trace of morphine, but narcotine and codeïne or thebaïne (*Repert.* 51, 211; 53, 289). — See *Handbuch* viii. *Phytochem.* 40.

Preparation. From Opium. A. When Morphine is the only or the principal product sought. — 20 parts of opium cut in slices are boiled in 60 parts water for half an hour, or until all the slices are opened out; the liquid is then strained, and the residue is squeezed and again twice treated with fresh water in the same way. The united extracts are boiled down to half their bulk, then stirred into a boiling lime-lye compound of 3 parts slaked lime and 40 parts water; the liquid is boiled for a quarter of an hour, and then strained; and the calcareous residue is pressed and again twice boiled in 50 parts water. The whole of the calcareous liquors are now boiled down to 40 parts and mixed at boiling heat with 2 parts sal-ammoniac; the heat is kept up for an hour, or as long as ammonia is given off; the liquid is then allowed to cool; and after 8 days the morphine which separates in the form of brown granules is collected : the mother-liquor yields another crop, if further boiled down and left to itself. The product may be purified by washing in cold water, solution in hydrochloric acid, repeated boiling with excess of milk of lime, and precipitation with sal-ammoniac. (Mohr's method, *Ann. Pharm.* 35, 120; *Repert.* 71, 289). This method is based upon the observations of Thiboumery, Couerbe & Pelletier, and is here given as described by Wittstein (*Repert.* 72, 336; *Preparation and testing*, Munich, 1845). — Couerbe precipitates the morphine from the lime-solution by hydrochloric acid (or by the passage of carbonic acid), but as thus obtained it is less crystalline than when precipitated by sal-ammoniac (Mohr). The morphine which is carried down by the carbonate of lime formed during the evaporation of the lime-solution, may be recovered by boiling with alcohol (Wittstein). Herzog therefore (*N. Br. Arch.* 33, 158), in the purification process, dissolves the morphine in a cold solution of potash, agitates the solution with animal charcoal, and precipitates with sal-ammoniac — The lime-residue yields thebaine to boiling alcohol (Thiboumery).

The numerous other methods of preparation differ from one another as regards the *extraction, precipitation,* and *purification* of the morphine.

1. *Extraction.* Cold, or more conveniently, boiling water deprives opium of the whole of its morphine (Biltz *N. Tr.* 23, 1, 292), (Mohr), so that the application of water containing acetic acid (Sertürner, Duflos, Winckler, Staples) or of water containing hydrochloric acid (Henry & Plisson, Wittstock, Zange, Merck), or of alcohol (Guillermond, Tilloy) as proposed by these chemists, appears to be superfluous. Still De Vry found (*N. J. Pharm.* 17, 439) that the whole of the morphine did not pass into the aqueous extract in the case of every sample of opium, and that in one case only a trace was extracted. Also, according to Sertürner, Berzelius & Petit, acids extract a certain quantity of morphine from opium-marc which has been exhausted with water. Alcohol or acids dissolve out the greater part of the narcotine, while, as a rule, after extraction with water, most of the narcotine remains in the residue (p. 136). — Robinet recommends extraction with water containing common salt. Bley & Diesel (*N. Br. Arch.* 39, 443) who in other respects give the preference to Mohr's method, use hydrochloric acid in making the extract, because the pressing and straining are

thereby rendered easier. Blondeau (*J. Chim. méd.* 6, 47 ; *Br. Arch.* 37, 108) sets the opium into fermentation after it has been soaked in water, by the addition of $\frac{1}{16}$th honey and some yeast, and does not strain off until the fermentation is complete. See the report on this process by Guibourt & Robiquet (*J. Chim. méd.* 10, 100).

2. *Precipitation.* Aqueous ammonia is usually employed to precipitate the extract of opium ; according to Winckler (*Repert.* 59, 5) it precipitates the morphine as completely as carbonate of soda does, but the ammonia which has been added in excess must be evaporated in an open basin at 50°. According to Thomson and others, the filtrate separated from the precipitate caused by ammonia, gives a further deposit of morphine on continued evaporation and addition of ammonia,—perhaps when the ammonia has been added in excess, or when the liquid, after the evaporation of the free ammonia, has been boiled long enough to decompose the sal-ammoniac. — Narcotine and some other bodies may either be removed before the precipitation of the morphine, or separated during the purification of the precipitate.

Berzelius (*Lehrbuch*, 3 Aufl. 6, 274) separates the narcotine in the first instance by evaporating the acetic acid extract, to dryness softening the residue with water, and boiling it with ether, which takes up the narcotine. More narcotine may be extracted from the residue by diluting it with a small quantity of water ; the solution is then filtered off, after which the morphine is dissolved in a larger quantity of water, and precipitated by ammonia. Fauré (*J. Pharm.* 15, 568) separates the narcotine by repeatedly concentrating the extract and redissolving, whereupon it separates together with resinous matter. — Wittstock (*Berzelius Lehrbuch*, 3 Aufl. 6, 276) saturates the hydrochloric acid extract with common salt ; the liquid then becomes milky, and after a few days deposits the narcotine in warty masses, while the morphine remains in solution (p. 137) ; a portion of the morphine is however very apt to go down with the narcotine (Wittstock, as reported by Mohr, *Repert.* 71, 292 ; Bischoff, *Mag. Pharm.* 27, 134). On the purification of morphine thus obtained, see Leverkohn (*Kastn. Arch.* 17, 127). — Duflos precipitates the colouring substances from the acetic acid extracts by neutral acetate of lead. and then proceeds according to Hottot's method ; or he dissolves in the watery extract of opium a quantity of bicarbonate of potash equal to $\frac{1}{8}$ the weight of the opium employed ; allows it to stand for some time ; filters off from the resulting precipitate containing narcotine ; boils the filtrate as long as carbonic acid continues to escape, and leaves it for 24 hours : the morphine then crystallises out (*N. Br. Arch.* 29, 68). A similar method of purifying morphine containing narcotine is adopted by Duflos (*Schw.* 61, 117). — Staples (*J. Pharm.* 14, 467 ; *J. Chim. méd.* 4, 496) adds alcohol to the extract of opium before precipitating with ammonia, probably in order to keep the resin and narcotine in solution. — Preuss (*Ann. Pharm.* 26, 93) concentrates the aqueous extract of opium to three times the weight of the opium employed, and precipitates it at the boiling heat with a large excess of ammonia ; the liquid becomes thick, pulpy, and glutinous, and forms a black, pitchy precipitate which must be removed from the liquid. The liquor freed from this precipitate deposits yellow crystals of morphine as the ammonia evaporates.

If extract of opium evaporated down till it marks 2° B. be mixed while yet somewhat warm, first with a small quantity of ammonia, so

as just to neutralise the liquid, a soft brown resin is deposited, so that if excess of ammonia be then added to the filtrate, a purer precipitate of morphine is obtained (Hottot, *J. Pharm.* 10, 475; *Schw.* 42, 461; Merck).—Compare Anichini (*Brugn.-Giorn.* 20, 7) The complete separation of the soft resin from the morphine takes place only when the extract of opium has not been previously treated with ether (Berzelius). — According to Girardin (*J. Pharm.* 14, 216) the precipitate produced by the first addition of ammonia, likewise contains a certain quantity of morphine, which is lost unless some further use is made of the precipitate. Guibourt & Robiquet (*J. Chim. méd.* 6, 101) found the purification of the first precipitate very difficult, whereas Dublane (*J. Chim. méd.* 4, 537) defends this method against Henry and Plisson, maintaining that, with the right proportion of ammonia, all the narcotine goes down with the resin. According to Pagenstecher (*N. Tr.* 3, 1, 357) also, ammonia precipitates chiefly narcotine at first. Papaverine appears (according to Merck's observations) to be contained in this first precipitate.

If in the precipitation of morphine, only sufficient ammonia is added to neutralise the liquid, part of the morphine is thrown down as a meconate: the ammonia must therefore be added in excess and the excess allowed to evaporate. Morphine which has been precipitated by ammonia from an alcoholic solution contains meconate of lime, which exists in the extract as an acid salt (Guibourt). If 3½ oz. solution of ammonia be added to an extract made from 15 oz. opium and 58 oz. alcohol, and the liquid filtered after half an hour, the crystalline precipitate will contain narcotine, but no morphine, which may easily be obtained pure from the filtrate (Ramdohr, *Pharm. Zeitschr.* 1854; *N. Repert.* 4, 33).

Robiquet employs magnesia instead of ammonia for the precipitation of extract of opium.—On the use of lime see above, and on that of potash, below; both, if employed in excess, redissolve the morphine which is at first precipitated.

3. *Purification.* Since morphine precipitated by ammonia contains or may contain colouring matter, resin, narcotine, thebaïne and papaverine, it must be purified by one of the following methods, in which, attention is (in most cases) chiefly directed to the separation of the narcotine,—that of the other substances, if it does not take place at the same time, being attained by recrystallisation from alcohol. Animal charcoal is to be avoided, as it takes up morphine; it appears however from Guthe's experiments, that the use of moist bone-black which has been cleansed with hydrochloric acid and not reburnt, is less objectionable than is commonly supposed, since he obtained by this method as much as 8⅔ p. c. morphine. The decoloration of the acid solution takes place more easily than that of the alcoholic (Guthe, *N. Br. Arch.* 69, 132).

a. When powdered morphine containing narcotine is warmed with water slightly acidulated with acetic (or hydrochloric) acid, till the liquor begins to redden litmus, the whole of the morphine dissolves and the narcotine remains on the filter (Pelletier; Robiquet, *J. Pharm.* 9, 530; Merck). The solution of the two bases in excess of acetic acid may also be evaporated down, the narcotine then losing its acid, and crystallising out, while the acetate of morphine remains for the most part undecomposed, and may be extracted with water (Merck).

b. If the precipitate is dissolved in water containing hydrochloric acid (or sulphuric acid according to Pelletier), hydrochlorate (or sulphate) of morphine crystallises out after concentration, while colouring

matter and narcotine remain in the mother-liquor, and may be removed by pressing the crystals (Lange; Wittstock). —Henry & Plisson (*J. Pharm.* 14, 241) and Gregory (*Edinb. Méd. and Surg. J.* 107, 331; *J. Pharm.* 19, 278) combine the two methods of purification (*a* and *b*), inasmuch as they warm the precipitated morphine in water containing a little hydrochloric acid, as long as the acid is thereby neutralised, filter from the narcotine and resin, and recrystallise the hydrochlorate.

c. When the hydrochloric acid solution of morphine and narcotine is supersaturated with solution of potash, the morphine is dissolved in the first instance—a small quantity of narcotine only in presence of a large quantity of potash, and after prolonged action; the liquid should be quickly filtered (Robiquet; Wittstock).

d. Ether extracts all or almost all the narcotine from finely powdered morphine. This method of purification does not succeed very well (Pelletier, Mohr.) Winckler (*Mag. Pharm.* 9, 281) uses ether-alcohol instead of ether.

e. When the ammonia precipitate, either dried or still moist, is drenched with alcohol of 65 p. c. and left to stand for twelve hours, the alcohol takes up very little morphine, but much colouring matter (Sertürner; Thomson, *Thoms. Ann.* 15, 473; *Schw.* 31, 486; Choulant, *Gilb.* 56, 343; 59, 412; Girardin, *J. Pharm.* 14, 246).—In this case, alcohol takes up morphine, narcotine, codeine and thebaïne (Pelletier). See below.

f. When crude morphine is dissolved in water containing hydrochloric acid, and a considerable excess of hydrochloric acid is added, a crystalline precipitate of hydrochlorate of morphine is formed. This is pressed, dissolved in hot water, with addition of $\frac{1}{3}$ as much alcohol as water, and precipitated by ammonia; and the precipitated laminæ are purified by a repetition of the process (Hirzel, *Pharm. Zeitschr.* 1851, 6; *Lieb. Kopp's Jahresber.* 1851, 467).

g. If the precipitated mixture of morphine and narcotine is washed, and then heated with water and a slight excess of sulphate of copper, the morphine dissolves as sulphate, with separation of terbasic sulphate of copper, which remains undissolved together with the narcotine. After filtration, the excess of copper-salt is precipitated by hydrosulphuric acid, and the morphine by ammonia (De Vry, *N. J. Pharm.* 17, 439).

If the morphine-precipitate contains opianyl, the latter may be extracted by agitation with ether, after supersaturation with hydrochloric acid (Pelletier).

B. *In case it is desired to obtain all the principal constituents of the opium.*
1. Robertson-Gregory's method.
Opium cut in small pieces is exhausted with water at 38°; the extract is evaporated down to a syrup, after the addition of powdered marble; excess of chloride of calcium is then added; and the whole is boiled for a few minutes. The liquid, when cold, is diluted with a moderate quantity of water, which throws down flakes of resin, together with meconate of lime and colouring matter; then filtered and evaporated to the crystallising point, with addition of a piece of

marble; and the remaining solution is poured off from the sediment. The crystals obtained after cooling and concentrating, are separated by pressure from the black mother-liquor (Robertson, *J. Pharm.* 19, 158; see also 19, 278). Couerbe concentrates the aqueous extract of opium, in winter to 10°, in summer to 15° and higher; adds chloride of calcium to the extent of ½th of the opium employed; then cools, collects, and presses the crystalline mass which has separated.

The crystals are a mixture of the hydrochlorates of *morphine* and *codeïne;* they become white by repeated crystallisation, and when dissolved in water, are decomposed by ammonia, whereby the morphine is precipitated, while the codeïne remains in solution, and may be separated by concentration and boiling with solution of potash (Robiquet, *N. J. Pharm.* 19, 160; *Ann. Pharm.* 4, 106).

Thebaïne and *narceïne* (also narcotine, papaverine, and opianyl) are obtained in the following way from the black mother-liquor expressed from the hydrochlorates of morphine and codeïne. *a.* The liquor is evaporated down to the consistence of treacle, and again diluted with water acidulated with hydrochloric acid; a black matter containing ulmin then rises to the surface, and may be removed with a skimming-ladle.

The clear liquor is mixed with ammonia, which throws down morphine and thebaïne as a black precipitate (to be separated by boiling ether after drying and pulverisation); and the filtrate, after being concentrated to a thin syrup, is violently shaken up with ether, in order to extract opianyl. The remaining black liquid solidifies, in the cold, to a crystalline mass, from separation of narceïne. In this way, 40 lbs. opium yielded 50 oz. morphine, 1½ oz. codeïne, 1 oz. thebaïne, 1 oz. opianyl, and 6 drachms narceïne (Couerbe, *Ann. Chim. Phys.* 59, 167).

b. The aqueous extract is diluted with water, filtered, and precipitated by ammonia; and the precipitate separated from the liquor (which contains narceïne) is dissolved in boiling alcohol; the alcoholic solution, on cooling, yields crystals of narcotine and papaverine. The mother-liquor leaves, on evaporation, a dark amorphous residue, containing all the thebaïne, together with a little narcotine and much resin. It is treated with hot acetic acid; basic acetate of lead is added in sufficient quantity to produce a distinct alkaline reaction; and the precipitate, which contains narcotine (papaverine?) and resin is separated from the solution containing the thebaïne, from which (after removal of the lead by sulphuric acid) the thebaïne is precipitated by ammonia. — The liquor containing narceïne (see above) is precipitated by neutral acetate of lead, filtered, freed from excess of lead by sulphuric acid, and neutralised with ammonia; on evaporation at a gentle heat, narceïne crystallises out (Anderson, *Ann. Pharm.* 86, 180). Opianyl and papaverine may still be obtained from the mother-liquor of the narceïne, by the method given in vol. xiv, p. 423, 3.

2. *Pelletier's method.* One kilogramme of Smyrna opium is worked up with the hand in 2 kilos. of cold water, the solid matter allowed to settle, the liquid decanted, and the sediment treated in this way four times, then washed with a jet of water and filtered. The aqueous solution is evaporated; the residue again taken up in water; and the solution is filtered from the undissolved narcotine, heated to 100°, mixed with

ammonia, and boiled for 10 minutes to expel the excess of ammonia. If it be now filtered while boiling hot, morphine remains on the filter, together with resin, while many nearly pure crystals of morphine form in the filtrate. If, on the other hand, the solution is allowed to cool slowly, crystals of morphine are obtained, enveloped in a crust of resin. This crust is treated with ether, which extracts narcotine, opianyl, and oily matters; as, however, it is difficult to extract the whole of the narcotine in this way, the morphine is converted into sulphate, crystallised in that form, and thereby separated from the uncrystallisable sulphate of narcotine, after which it may be precipitated from the sulphate. —The liquor from which the greater part of the morphine has been separated by ammonia, still deposits a small quantity on evaporation. This is collected, and baryta-water is added to the filtrate, which precipitates meconic acid and brown colouring matter; these are separated by boiling alcohol. — The filtrate containing baryta is freed from that substance by carbonate of ammonia, and evaporated down to a thick syrup, which, after standing several days in the cold, solidifies to a pulpy mass of crystals.

This mass is drained and strongly pressed between linen, and the press-cake is boiled with alcohol of 40°, whereby narceïne is extracted, which may be purified by frequent crystallisation from hot water or alcohol, with help of animal charcoal. If it also contains opianyl, this substance may be extracted by treatment with ether. — The rest of the opianyl remains: *a.* In the mother-liquor expressed from the narceine; *b.* in the mother-liquor left after the recrystallisation of the narceine; and *c.* in the portion of the press-cake which did not dissolve in the alcohol. It is extracted from each of these materials by shaking up with ether; but that from *a* requires further purification by solution in boiling water, whereby portions of fat and narcotine taken up at the same time by the ether, are left undissolved, and may then be separated by hydrochloric acid. The portion of the press-cake (*c*) which was undissolved by alcohol, having been thus freed from opianyl, dissolves when drenched with water, with the exception of a little opium-marc; the aqueous solution contains an acid, some brown colouring matter, and gum (Pelletier).

Since it happens in this process that the liquor from which morphine, meconic acid, and the excess of baryta have been separated, becomes mouldy after being evaporated down to a syrup, or if further concentrated, refuses to crystallise, from being too glutinous, Pelletier proceeds with it as follows, in order to obtain morphine, codeïne, narceïne, and opianyl (*J. Pharm.* 21, 557; *Ann. Pharm.* 16, 27). He supersaturates with hydrochloric acid, and evaporates down to a syrup, then leaves it to stand in the cold till it sets to a crystalline pulp. This he presses, and purifies the crystals by solution in warm alcohol of 36° B.,—which leaves caoutchouc and extractive matter undissolved,—then by repeated crystallisation from alcohol, and decolorisation of the aqueous solution by charcoal. The crystals thus obtained contain morphine, codeïne, narceïne, as hydrochlorates, together with opianyl, the same bodies remaining also in the expressed mother-liquor. *a.* These *crystals* are treated with water at 50° until $\frac{9}{10}$ths is dissolved, leaving $\frac{1}{10}$th, principally narceine, undissolved. This is freed from adhering hydrochlorate of morphine by recrystallisation from boiling water, and from a trace of opianyl by ether. — The solution of the $\frac{9}{10}$ths is evaporated down and freed from opianyl by ether; the hydro-

chlorates of morphine and codeïne then remain, and may be separated by ammonia and potash. — b. The expressed black *mother-liquor*, when evaporated down to a soft extract and mixed with alcohol of 24° B., deposits ammonia-salts, potash-salts, and extractive matters, which are separated by filtration. The filtrate again mixed with alcohol, but of 38° to 40°, deposits a black substance, which carries down the narceïne, to be separated by boiling with alcohol. Morphine, codeïne, and opianyl still remain in the filtrate, and may be separated as above.

Opium-marc, which has been exhausted with cold water, behaves to ether just like the opium in its original state, yielding narcotine, fat (or soft resin), and caoutchouc. When it is exhausted with warm alcohol of 36°, gum, opium-resin, fat, and especially narcotine, are taken up, and after this treatment, ether extracts fat, narcotine, and caoutchouc. The residue then left yields nothing to rock-oil, and water extracts from it only a trace of gum, while woody fibre and bassorin remain behind (Pelletier, *Ann. Chim. Phys.* 50, 240).

3. Merck (who starts with the view that codeïne and thebaïne occur in opium as salts, and in this state are not soluble in ether): 1. Exhausts powdered opium with boiling ether, which extracts narcotine, opianyl, and glutinous matters. 2. Warms the residue with a little water and carbonate of potash, and afterwards boils it out with ether, whereby codeïne, thebaïne, porphyroxine, and caoutchouc are obtained in solution. 3. Boils in alcohol the opium which has already been twice treated with ether, in order to obtain the morphine. The residue obtained by evaporating the first ethereal extract, yields opianyl to boiling water, and narcotine to boiling alcohol. — On evaporating the second ethereal extract and drenching the residue with dilute hydrochloric acid, resin separates out, while codeïne, thebaïne, and porphyroxine are dissolved, and may be separated by ammonia, which precipitates only the thebaïne and porphyroxine. The codeïne is precipitated from the ammoniacal filtrate by caustic potash. The thebaïne and porphyroxine on the other hand are dissolved in ether, the solution is evaporated, and the residue drenched with alcohol, which quickly dissolves the porphyroxine, leaving the thebaïne. — The morphine of the alcoholic extract is obtained by evaporation, solution in dilute acetic acid, and precipitation with ammonia (Merck, *Ann. Pharm.* 21, 201).

4. Riegel exhausts pulverised opium successively with boiling ether and water, and thus obtains an ethereal solution containing opianyl, narcotine and porphyroxine (together with caoutchouc, resin and fat); and an aqueous solution which yields morphine, codeïne, meconic acid, thebaïne and narceïne.

a. *Treatment of the ethereal solution.* The ether is distilled off and the brown saline mass well boiled with water, which takes up chiefly the *opianyl*, to be purified by repeated solution in ether and water. The ethereal extract which has been exhausted with water yields narcotine and porphyroxine to boiling alcohol, while caoutchouc, resin and fat remain undissolved. In order to separate the narcotine from the porphyroxine, the alcoholic extract is brought to the crystallising point; the crystals are dissolved in boiling alcohol (containing hydrochloric acid? Kr.) and precipitated by ammonia; the precipitate is dissolved in

dilute hydrochloric acid; and the solution is evaporated down to a syrup, which, on standing for some time in a dry place, solidifies to a mass of needle-shaped crystals, from which *narcotine* can be obtained. The expressed mother-liquor treated with excess of ammonia gives a precipitate, whose alcoholic solution crystallises on evaporation in shining needles of *porphyroxine*.

b. *Treatment of the aqueous solution.* The concentrated solution is mixed with a quantity of chloride of calcium equal to ⅓th of the opium employed, then boiled for some time and left to cool; and the crystalline mass (a) consisting of meconate of lime, hydrochlorate of morphine, and codeïne which separates out, is collected. On digesting this mass in cold water, *meconate of lime* remains behind: the aqueous solution concentrated and neutralised at the same time with carbonate of potash, yields an additional quantity of meconate of lime, and after the separation of this salt, solidifies to a crystalline mass of hydrochlorate of *morphine* and codeïne, which may be separated by ammonia. The black syrup separated from the crystalline mass is diluted with water acidulated with hydrochloric acid, filtered from a resinous gum, and precipitated with ammonia, which throws down *morphine* and *thebaïne*; these may be separated by ether, which takes up the latter. The ammoniacal filtrate evaporated down and cooled, yields crystals of narceïne (Riegel, *Jahrb. pr. Pharm.* 11, 103).

Estimation of Morphine in Opium. 15 grammes of opium cut in pieces are triturated with 60 grms. alcohol of 71 p. c.; the solution is strained through linen; and the residue, after being pressed, is again treated in the same way with 40 grms. alcohol. The alcoholic tincture mixed with 4 grms. of aqueous ammonia yields in 12 hours crystals of morphine and narcotine, which are collected, washed several times with water, and stirred up in the water; the crystals of morphine then sink to the bottom, while those of narcotine, being lighter, remain longer suspended and may be separated by decantation (Guillermond, *N. J. Pharm.* 16, 17; *Pharm. Centr.* 1849, 720; *Lieb. Kopp's, Jahresb.* 1849, 607). Riegel (*Jahrb. pr. Pharm.* 23, 202), removes the narcotine precipitated together with the morphine, by washing with ether or with chloroform. Since the quantity of alcohol employed by Guillermond is not sufficient for the exhaustion of the opium, and as 12 hours is not time enough for complete crystallisation (Reveil; Guibourt), the latter treats dry powdered opium, or the aqueous extract of opium, with alcohol, either warm or cold, allowing it in either case to stand in the cold for 24 hours, to permit the separation of the resin, the wax, and a portion of the narcotine. The tincture is drawn off with a pipette, the residue washed with alcohol, and the entire liquid precipitated by a slight excess of ammonia. After evaporation of the excess of ammonia, the morphine is allowed to crystallise out completely, then collected and washed with alcohol of 50 p. c., afterwards with alcohol of 40 p. c., and finally with ether. The extract prepared with cold water from 20 or 30 grms. of opium, may also be redissolved in cold water; the solution precipitated by ammonia; and the precipitate collected after 36 hours, washed with cold water, then with alcohol of 40 or 50 p. c., and crystallised from boiling alcohol of 85 p. c. (Guibourt)

On the estimation of morphine, see further: Fordos (*Compt. rend.* 44, 1256;

N. J. Pharm. 32, 101 ; *Chem. Centr.* 1857, 589; *Kopp's Jahresb.* 1857, 603) ; Meurein (*N. J. Pharm.* 23, 176 and 262) ; L. Kieffer (*Ann. Pharm.* 103, 271 ; abstr. *J. pr. Chem.* 73, 55 ; *Chem. Centr.* 1857, 925 ; *N. J. Pharm.* 32, 455) ; A. Petit (*N. J. Pharm.* 43, 45) ; on an older process by Guillermond, see *J. Pharm.* 14, 436.
On the detection and identification of morphine in cases of poisoning, see Lassaigne (*Ann. Chim. Phys.* 25, 102) ; Mermer (*J. Chim. méd.* 23, 12) ; Stas (*N. J. Pharm.* 22, 281; *J. pr. Chem.* 55, 232; *Jahr. pr. Pharm.* 24, 313 ; *Lieb. Kopp's Jahresb.* 1851, 640) ; Flandin (*Compt. rend.* 36, 517 ; *J. pr. Chem.* 59, 185) ; Otto (*Ann. Pharm.* 100, 46) ; v. Uslar & J. Erdmann (*Ann. Pharm.* 120, 121 ; *Zeitschr. Chem. Pharm.* 5, 13) ; J. Erdmann (*Ann. Pharm.* 122, 360 ; *Zeitschr. Chem. Pharm.* 5, 466).

Properties. Crystallised morphine (see below) gives off water at a temperature of 120°, becoming anhydrous, and then melts easily to a colourless oil which solidifies to a crystalline mass on cooling (Sertürner, Duflos). It has neither taste nor smell (Sertürner); when finely powdered (or in solution) it is very bitter (Geiger). Its action is strongly narcotic. According to Lefort, when continued doses are given, it passes into the urine; according to J. Erdmann, when large doses are given, it is found in the stomach and intestines, but after smaller doses, it appears to be decomposed in the body, so that only traces of it can be recovered (*Ann. Pharm.* 122, 360). In opium-smoking, a portion of the morphine is volatilised undecomposed (Descharmes & Benard *Compt. rend.* 40, 34). In a hot aqueous or alcoholic solution, it exhibits an alkaline reaction with turmeric, rhubarb, Brazil-wood and reddened litmus (Sertürner), but it does not turn the tincture of mallows green (Guibourt, *J. Pharm.* 9, 382). — Molecular rotation to the left, in a sulphuric, hydrochloric or nitric acid solution $[\alpha] r = 89.8°$; nearly as great in an alcoholic, less in an ammoniacal ($[\alpha] r = 71.47°$) or in an alkaline solution ($[\alpha] r = 45.22°$) (Bouchardat, *N. Ann. Chim. Phys.* 9, 221).

		Dried.		Pelletier & Dumas.		Regnault.
34	C	204	71·58	71·13	71·65
	N	14	4·91	5·53	5·01
19	H	19	6·67	7·61	6·85
6	O	48	16·84	15·73	16·49
C³⁴NH¹⁹O⁶		285	100·00	100·00	100·00

		Liebig.	Henry & Plisson.	Will.	Laurent.
34	C	71·37	71·60	71·40	71·61
	N	4·99	4·72		
19	H	6·37	6·80	6·72	6·62
6	O	17·27	16·83		
C³⁴NH¹⁹O⁶		100·00	100·00		

So, according to Laurent,—Liebig's formula contains 1 at. hydrogen less. — Regnault's formula is C³⁵NH²⁰O⁶. — Isomeric with piperine (xv. 18).

Decompositions. 1. Morphine yields, by *dry distillation*, carbonate of ammonia, empyreumatic oil, and charcoal (Seguin).—2. When heated above its melting point, it assumes a purple colour (Merck), and solidifies on cooling to a black resinous mass (Braconnot); when heated still more strongly in the air, it gives off vapours having a resinous odour, and then *burns* quickly, with a bright red and very sooty flame, leaving

behind a bulky and very combustible charcoal. — 3. A salt of morphine dissolved in water is decomposed by a *current of electricity*, as violently as by hot concentrated nitric acid (Rochleder & Hlasiwetz, *Wien. Akad. Ber.* 4, 477). — 4. Morphine and *sulphur* melted together, give off hydrosulphuric acid at the moment of combination (Sertürner).

5. When morphine is triturated with *iodine*, reddish-brown mixtures are formed, consisting perhaps of iodide of morphine, which do not smell of iodine. After some hours, the colour changes to violet-brown, then to black; the odour of iodine is given off; and the mixture contains hydriodate of morphine, together with a product of the decomposition of morphine (Pelletier).

The violet-brown mixture does not dissolve in cold water; with $\frac{1}{4}$th part of iodine, it forms a neutral solution in a large quantity of boiling water, and with $\frac{1}{2}$ part of iodine, an acid solution containing a large quantity of hydriodate of morphine. With equal quantities of morphine and iodine, an acid mass is obtained, which is completely soluble in boiling alcohol, the solution yielding by spontaneous evaporation, first a red-brown substance, and afterwards crystals of hydriodate of morphine. The red-brown substance contains 35·34 p. c. iodine [accordingly Gerhardt (*Traité*, 4, 38) gives it the formula $2C^{34}NH^{19}O^6,3I$; calculation = 40·1 p. c. I.]; it dissolves in dilute acids and alkalis only on boiling, and is reprecipitated on cooling. When treated with hydrosulphuric acid, under water, the greater part dissolves, forming a limpid solution, but is thrown down again on evaporation; ammonia forms a scanty bitter precipitate free from morphine, and colours the liquid dull red. When triturated with alcohol and mercury, it forms mercurous iodide, from which alcohol takes up organic matter and mercuric iodide. — Iodine forms similar products with sulphate of morphine; so likewise does chlorine when passed into hydriodate of morphine (Pelletier, *Ann. Chim.Phys.* 63, 185; *Ann. Pharm.* 22, 120). — Morphine is coloured reddish-yellow in vapour of iodine (Donné); acetate of morphine is coloured russet-brown by trituration with $\frac{1}{10}$th iodine (Voget); aqueous acetate of morphine forms, with a small quantity of tincture of iodine, a brownish-red precipitate, which disappears when stirred; with a large quantity of the tincture, it yields a copious, sparingly soluble precipitate (Merck). Cold aqueous morphine is not altered by iodine-water (Duflos).

6. In *bromine-vapour*, morphine assumes a pale orange-yellow colour (Donné). In solutions containing 1 p. c. or more of morphine, bromine-water forms a yellow precipitate, which disappears on agitation, colouring the liquid pale yellow (Duflos). Acetate of morphine is altered by tincture of bromine (Merck); aqueous solution of morphine is not altered by bromine-water (Duflos).

7. *Chlorine-gas* passed through water in which morphine is suspended, colours it first orange-yellow, then bright red, and dissolves it; a larger quantity of chlorine again colours the red liquor yellow, and separates flakes containing resin and a black substance, while ammonia forms scarcely any precipitate in the filtrate (Pelletier, *J. Pharm.* 24, 164; *Ann. Pharm.* 29, 56). Morphine dissolves in chlorine-water, with yellow colour, which is changed by ammonia to a dark brownish-red, without precipitation (Braconnot). Aqueous salts of

morphine are coloured in the same manner by chlorine (Lepage, *J. Pharm.* 26, 140; Soubeiran & Henry, *J. Pharm.* 22, 134); but cold aqueous morphine (Duflos) and acetate of morphine dissolved in 500 parts of water (Merck) are not changed by chlorine-water. Sulphide of ammonium causes the yellow colour partly to disappear (Duflos). — Aqueous *chloride of lime* colours morphine yellow, then quickly violet-brown, on further addition again yellow, and dissolves it an altered state (Robinet); it colours morphine-salts dark orange (Duflos). — Morphine is coloured brown-yellow by the vapour of *chloride of iodine* (Donné).

8. Morphine kept in contact with *ammonia* for a considerable time, absorbs oxygen and decomposes (Guibourt). The solution in ammonia, and still sooner that in soda-ley, assumes a dark brown colour (Bouchardat). The solution in *potash-ley* becomes brown when heated; on evaporation it acquires a red, and ultimately vermillion-red colour, swells up, emitting the odour of burnt horn, and leaves charcoal containing cyanide of potassium (Duflos). Excess of hydrate of potash, at 200°, generates methylamine (Wertheim, *Wien. Akad. Ber.* 4, 33; *Ann. Pharm.* 73, 210).

9. Morphine does not become coloured when cold oil of vitriol is poured over it (Riegel. Fresenius, Guy); it assumes a dirty yellow or grey colour (Merck, Schlienkamp), brown when heated (Guy). It dissolves quickly in oil of vitriol, with a green, dirty grey, brown, or wine-red colour, according to the temperature; to produce the red colour, requires the greatest degree of heat, with addition of water (Duflos). When morphine is added to hot oil of vitriol, a large quantity of sulphurous acid is given off, and a viscid liquid formed, which loses its colour on addition of water, and deposits a black powder (Duflos). — Morphine heated with excess of dilute sulphuric acid, or with anhydrous sulphuric acid, is converted into sulphomorphide (Arppe).

10. Concentrated *nitric acid* colours morphine red, then yellow (Pelletier & Caventou), yellowish-red (Lassaigne, Schlienkamp, Riegel), ruby-red (Merck); first saffron-yellow, then hyacinth-red, which colour is made darker by carbonate of soda (Duflos). Aqueous morphine-salts are coloured yellow by nitric acid, orange-yellow when heated, lighter on boiling (v. Planta); cold aqueous morphine becomes orange-coloured when heated with nitric acid (Duflos). The nitric acid solution is decolorised by hydrosulphuric acid or sulphide of ammonium (Hünefeld, *Schw.* 60, 453); protochloride of tin colours it red-brown (v. Planta). — Nitric acid forms oxalic acid from morphine (Seguin), but no picric acid (Liebig). It forms, as with narcotine (p. 140), resinous products, from which potash-ley eliminates methylamine (Anderson).

11. *Nitrous acid* forms three basic products, according to the time for which it is allowed to act: C³⁴NH²¹O⁸ + 2Aq., C³⁴NH¹⁹O⁸, and C³⁴NH²¹O¹⁰ (Schützenberger, *Compt. rend.* 46, 598; *Ann. Pharm.* 108, 346).

Oil of vitriol containing a little nitric acid colours morphine brown-green; with only a trace of nitric acid, the colour is brownish (Couerbe). When 8 or 10 drops of oil of vitriol containing nitric acid, prepared as directed at page 141, are added to morphine, it assumes a violet-red

colour; the addition of 2 or 3 drops of water assists the development of the colour. If a few fragments of peroxide of manganese (or chromate of potash: *Otto*) are added, the colour, after an hour, becomes mahogany-brown, changing to dirty yellow on careful dilution with water and almost complete neutralisation with ammonia, or to brownish-red if the ammonia is in slight excess (J. Erdmann). A very dilute solution of morphine, which does not show any colour with nitric acid, becomes red it oil of vitriol is also added. A solution of morphine in oil of vitriol is also reddened by saltpetre or by antimonate of potash (Lefort, *Rev. scient.* 16, 355).

12. *Iodic acid* colours morphine and its salts immediately brownish-red, with separation and precipitation of iodine (Serullas, Duflos). Even $\frac{1}{100}$ grain acetate of morphine shows this colour, or the blue colour of iodide of starch if a little paste is mixed with it; in dilute solutions the reaction is slower; but it is visible even in 7,000 parts of water. The same reaction is exhibited by biniodate of potash and its combination with chloride of potassium or bisulphate of potash (ii. 71), but not by neutral iodate of potash, except in presence of sulphuric acid (Serullas), or when acetate of morphine is used (Simon, *Repert.* 65, 205). Tinctures of opium, or mixtures of morphine with other alkaloids, likewise exhibit this reaction (Serullas). The presence of *prussic acid* does not interfere with it (Millon, *N. Ann. Chim. Phys.* 13, 57). In dilute solutions of morphine, the colour is plainer after addition of oil of vitriol (Lefort). — Ammonia deepens the colour of a mixture of iodic acid and morphine, so that $\frac{1}{10000}$ morphine can then be recognised (Lefort, *N. J. Pharm.* 40, 97; *Anal. Zeitschr.* 1, 134).

When a mixture of morphine and iodic acid is diluted with water, the solution poured off from the iodine appears reddish-brown, but becomes light yellow as the iodine volatilises, and leaves on evaporation a *light-yellow crystalline powder*, which can be freed from excess of iodic acid by washing. This powder swells up when thrown on glowing coals or heated in a tube to 125°, giving off iodine and leaving charcoal, together with a brown substance which dissolves with brown colour in ammonia. It is sparingly soluble in water, but in a few minutes both the substance itself and the water become rose-coloured, without any liberation of iodine. Sulphurous acid at first separates iodine, which redissolves in excess of the acid; the colourless liquid assumes a beautiful rose colour on addition of potash or ammonia, but it is again bleached by sulphurous acid. — Oil of vitriol liberates iodine from the yellow powder, which therefore contains an iodate, together with hydriodic acid (Serullas, *Ann. Chim. Phys.* 43, 211: *Pogg.* 18, 119). Compare Pelletier, *Ann. Chim. Phys.* 63, 192.

13. Morphine is decomposed by *periodic acid*, with separation of iodine (Bödeker, *Ann. Pharm.* 71, 64). A portion of the liberated iodine then forms hydriodate of morphine (Langlois, *N. Ann. Chim. Phys.* 34, 278). — 14. *Bromic acid* is coloured yellow by morphine, becoming darker on evaporation, without formation of crystals (Serullas, *Ann. Chim. Phys.* 45, 278). Bromate of potash has no action on morphine-salts, and colours them only faintly yellow on addition of sulphuric acid (Simon, Duflos). — 15. *Chloric acid* produces no coloration in the cold, but a golden-yellow colour at the boiling heat (Duflos).

16. *Chromate of potash* colours a solution of morphine in oil of vitriol brownish-green, quickly changing to emerald-green, with evolution of gas (Riegel, Eboli); it reduces manganic sulphate to manganous sulphate, and permanganate of potash to manganic acid (Lefort); the latter turns the solution of morphine brown, and then bleaches it (Guy, *Anal. Zeitschr.* 1, 92). Cold aqueous morphine colours permanganate of potash green (Duflos). — 17. Morphine is coloured dirty-brown by oil of vitriol and *peroxide of lead* (Riegel); red by dilute sulphuric acid and peroxide of lead (Lefort); on boiling the solution as long as effervescence continues, the morphine is converted into an amorphous, yellow, deliquescent, acid body, Marchand's *morphétine* (E. Marchand, *J. Chim. méd.* 20, 365).

18. Aqueous *ferric hydrochlorate* dissolves morphine with blue colour, and colours aqueous morphine or its salts bright blue; the blue colour is destroyed by acids, even by distilled vinegar, also by alcohol and ether-alcohol, but not by ether free from alcohol, whereas alkalis render it deeper (Robinet). According to Merck, the solution deposits sesqui-oxide of iron, and yields crystals of hydrochlorate of morphine. — Morphine is not coloured by all ferric salts; the finest colour is produced by the hydrochlorate and nitrate; none by the hydriodate, acetate, tartrate or citrate (Fuchs, *Zeitschr. Phys. v. W.* 6, 88).
When morphine is drenched with a very concentrated solution of ferric chloride, made as neutral as possible, the mixture, which at first is dark-blue, gradually turns paler, and solidifies after 24 hours to a dirty white mass of crystals of hydrochlorate of morphine, without separation of ferric oxide. Water restores the blue colour of the mixture and dissolves it, colouring the mother-liquor rose-red after separation of the crystals, and forming a solution which, if kept excluded from the air, is permanent, and does not deposit any oxide of iron. When the mother-liquor is evaporated down, there remains a brown deliquescent matter, which is partially soluble in alcohol, the remainder dissolving with violet colour in water. By evaporating the alcoholic solution, digesting the residue in ether, and evaporating again, a small quantity of minute greenish translucent crystals is obtained, —together with chloride of iron—which dissolve in water with a fine blue colour, and even in small quantity colour a large quantity of water; so that they are probably the cause of the blue coloration (Pelletier, *Ann. Chim. Phys.* 50, 272; *Ann. Pharm.* 5, 172).

19. A cold solution of morphine or of its salts reduces *nitrate of silver*, even in the dark (Duflos). The reduction takes place even in very dilute solutions; after the reduced silver has been separated, strong nitric acid colours the filtrate orange-violet (Horsley, *Anal. Zeitschr.* 1, 517). The salts of morphine separate oxide of silver from a solution of argentate of ammonia, and reduce it to the metallic state, even in diffused light (Kieffer). — 20. Morphine-salts give, with solution of *chloride of gold*, a yellow precipitate, which dissolves with green colour in excess of the morphine-salt, and in hydrochloric acid, but soon changes to a deep blue and violet, owing to the separation of metallic gold, which is visible even in very dilute solutions (Merck; Duflos; Larocque, *J. Chim. méd.* 18, 696; Riegel). — 21. Morphine heated to the boiling point with *bichloride of platinum*, forms a very dark, almost black mixture, which contains the platinum-salt of

a new base and a dark-brown granular acid, the latter being insoluble in water, alcohol, and ether, soluble in ammonia and potash, and forming an insoluble salt with oxide of silver (Blyth, *Ann. Pharm.* 50, 52).

22. In an alkaline solution it reduces an equivalent quantity of *red prussiate of potash* to yellow prussiate (Kieffer). On this reaction Kieffer bases a volumetric determination of morphine; but according to Mohr (*Titrirbuch*, 2nd edit. p. 523), the decomposition does not go on rapidly enough, the rate varying with the temperature of the solution and the amount of red prussiate of potash in excess.

23. *Iodide of methyl* and *iodide of ethyl*, heated with morphine, form hydriodate of methyl- and ethyl-morphine. — A mixture of crystallised morphine with *chloride of amyl* and alcohol, remains unchanged when heated for three days to 100°, but after from five to fourteen days' heating, it deposits crystals of hydrochlorate of morphine (How, *Chem. Soc. Qu. J.* 6, 125; *Ann. Pharm.* 88, 336).

$$C^{34}NH^{19}O^6,2HO + C^{10}H^{11}Cl = C^{34}NH^{19}O^6,HCl + C^{10}H^{12}O^{2\cdot}$$
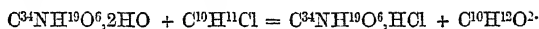
24. Morphine does not decompose in a fermenting solution of sugar (Larocque & Thibierge, *J. Chim. méd.* 18, 689).

Combinations. — A. *With Water* — a. *Crystallised Morphine.* White, translucent, or nearly transparent, chiefly short prisms, belonging to the right prismatic system. Fig. 53, without a, i, t, and p. A rhombic prism, $y : y = 127°\ 20'$, having its acute lateral edges symmetrically truncated by m. $y : m = 116°\ 20'$; on these faces rests the bevelling-face u. $u : u$ above = $95°\ 20'$; $u : u$ over $m = 84°\ 40'$; $u : m = 132°\ 20'$. Cleavable parallel to m (Brooke, *Phil. Ann.* 6, 118). — $y : m = 116°\ 33\cdot5'$; $y : y = 126°\ 54'$, but instead of u, an obtuser bevelling, the two faces of which meet above at an angle of $130°\ 11\cdot5'$. The crystals are mostly short prisms, more rarely needle-shaped, sometimes also of octahedral habit.

Crystallised morphine is permanent in the air, and undergoes no alteration at 100°; according to Liebig, it loses 5·95 p. c. water at 120°, becoming thick and opaque; according to Regnault, 5·99 p. c. (2 at. = 5·71 p. c HO)

b. *Aqueous solution.* — Morphine dissolves in 1000 pts. cold water (Duflos), in 960 pts. at 18¾° (Abl). According to Duflos, it dissolves in 400 pts.; according to Merck, in 500 pts. boiling water.

B. *With Acids.* — Morphine dissolves freely even in dilute acids, forming perfectly neutral salts. It decomposes certain lead, iron, copper, and mercury salts, combining with their acids. From neutral sulphate (and acetate: *Duflos*) of copper, morphine throws down a basic sulphate, a portion of the copper, however, remaining in solution (Geiger, *Mag. Pharm.* 19, 154). — Most morphine-salts are crystallisable, inodorous, very bitter, and poisonous. According to Lassaigne & Feneulle, they deposit, in the circuit of a voltaic battery, needles of morphine at the negative pole, and the acid at the positive pole. They exhibit the reactions above described. — Their aqueous solutions, mixed with ammonia, a fixed alkali, baryta, lime, or magnesia, deposit morphine as a crystalline powder, soluble in excess of the

precipitant, except in the case of magnesia — difficult of solution, how-
ever, in excess of ammonia. According to Anderson (*N. J. Pharm.*
13, 443), the precipitate formed by ammonia is composed of micro-
scopic rhombohedral crystals. The salts are precipitated by the mono-
carbonates of the alkalis, and the precipitate is not redissolved in
excess. The alkaline bicarbonates precipitate only a portion of the
morphine from neutral morphine-salts; they do not precipitate acid
solutions in the cold (Duflos, Fresenius). Tartaric acid prevents pre-
cipitation by the alkaline bicarbonates (Oppermann, *Compt. rend.* 21, 810;
Riegel). — Morphine-salts dissolve in water and alcohol, not in ether
or in fusel-oil.

Carbonate of Morphine. — The carbonates and bicarbonates of the
alkalis added to solutions of morphine-salts, precipitate morphine free
from carbonic acid (Lange, Sertürner, How, Langlois). A solution
obtained in the preparation of morphine from opium, heated with bicarbonate of
potash to the boiling-point, and left to itself for twenty-four hours, deposited on one
occasion, grains of carbonate of morphine resembling poppy-seeds; but they could not
be obtained a second time (Kruger, *N. Br. Arch.* 49, 31). — Water saturated
with carbonic acid under pressure dissolves morphine, and on exposure
to a low temperature, deposits it as carbonate in short prisms, which
should be at once removed from the liquid. The salt, when heated,
gives off carbonic acid and water, leaving morphine. It dissolves in
4 parts of water, and precipitates acetate of lead (Choulant). —
Freshly precipitated morphine, suspended in water, is dissolved on the
passage of carbonic acid gas; the solution, cooled with ice and exposed
to the air, deposits crystals of morphine free from carbonic acid (How;
Langlois, *N. Ann. Chim. Phys.* 48, 502). — By decomposing hydro-
chlorate of morphine with carbonate of silver, an easily decomposible
carbonate of morphine is obtained (How, *Lieb. Kopp's Jahresb.* 1854,
518).

Phosphate of Morphine. — The neutral salt forms cubes, the acid salt
crystalline tufts (Pettenkofer, *Repert.* 4, 45). Bisodic phosphate added
to hydrochlorate or sulphate of morphine, throws down a finely inter-
laced crystalline precipitate, very soluble in hydrochloric acid
(v. Planta).

Hyposulphite of Morphine. — Sulphide of ammonium is added to an
alcoholic solution of morphine, and the mixture exposed to the air for
many hours or days; or a salt of morphine is decomposed by hypo-
sulphite of soda. — Silky needles (C³⁴NH¹⁹O⁶,HO,S²O² + 4Aq. It gives off
2 at. water at 100°. — Dissolves in 32 parts of cold water, and in 1050
parts of cold alcohol (H. How, *Edinb. New Phil. Journ.*, new series, 1, 47);
Pharm. Centr. 1855, 93; *Lieb. Kopp's Jahresber.* 1855, 571).

Sulphate of Morphine. — a. *Mono-acid.* Needles grouped in tufts
(Sertürner, Buchholz). At 120° they lose 9·64 p. c. water (Liebig)
(4 at. = 9·73 HO); at 130°, 11·59 p. c. (Regnault) (5 at. = 11·87 HO); the
dry salt is hygroscopic (Liebig). — It dissolves in 2 parts of water
(Choulant).

		Dried.			Regnault.	Pelletier & Caventou.		Robiquet.
34	C	204		61·08	60·59			
	N	14		4·20				
20	H	20		5·99	6·48			
7	O	56		16·76				
	SO³	40		11·97		11·08		12·8

C³⁴NH¹⁹O⁶,HO,SO³ 334 .... 100·00

			Crystallised.			Liebig.
34	C	204		53·83		53·81
	N	14		3·69		
25	H	25		6·60		6·52
12	O	96		25·33		
	SO³	40		10·55		10·72

C³⁴NH¹⁹O⁶,HO,SO³ + 5Aq. .... 379 .... 100·00

b. *Bi-acid.* — When the salt *a* is supersaturated with sulphuric acid, the solution evaporated down, and the excess of sulphuric acid removed with ether, there remains a salt which is very sour to the taste, and contains twice as much acid as *a* (Pelletier & Caventou).

Hydriodate of Morphine. — 1. Prepared by dissolving morphine in hydriodic acid. White, silky salt, rather freely soluble in water (Pelletier, *Ann. Chim. Phys.* 63, 193). — 2. Iodide of potassium added to a concentrated solution of acetate (hydrochlorate or sulphate: *v. Planta,*) of morphine, throws down crystals after standing some time (Merck). — Transparent, brilliant, slender needles, or four-sided prisms. Dissolves very sparingly in cold water, more easily in hot water and in alcohol. Contains 28·6 p. c. iodine (Winkler, *Jahrb. pr. Pharm.* 20, 323). C³⁴NH¹⁹O⁶,HI = 28·33 p.c. I.
Morphine is completely precipitated by *biniodide of potassium* (Wagner, *Chem. Centr.* 1861, 941). Comp. vii. 183.

Chlorate of Morphine. — Obtained by dissolving morphine in warm aqueous chloric acid. — Long, slender needles. Decomposed suddenly by heat, swelling up and carbonising (Serullas, *Ann. Chim. Phys.* 45, 279 ; *Pogg*, 20, 595).

Perchlorate of Morphine. — Obtained by neutralising morphine with aqueous perchloric acid. — White silky tufts of needles, which melt at 150° and then give off 8·34 p. c. water. Swells up when heated strongly. — Dissolves in water and in alcohol (Bödeker, *Ann. Pharm.* 71, 63).

					Bödeker.
C³⁴NH¹⁹O⁶,HO	306·0		70·59		70·58
ClO⁷	91·5		21·11		21·08
4HO	36·0		8·30		8 34

C³⁴NH¹⁹O⁶,ClHO⁸ + 4Aq. 433·5 .... 100·00 .... 100·00

Hydrochlorate of Morphine. — 100 pts. morphine absorb 12·67 parts hydrochloric acid gas (Liebig), 12·58 parts at 140° (Regnault), (1 at. = 12·28 HCl.). — Morphine does not dissolve perceptibly in cold concentrated hydrochloric acid. On addition of water, thick curdy flakes are formed, which dissolve in a larger quantity of water (Geiger). Aqueous acetate of morphine solidifies almost immediately on the

addition of common salt, owing to the formation of hydrochlorate of morphine (Robinet, Merck). When hydrochloric acid at 80° is saturated with morphine, the neutral liquid becomes acid on cooling, even before the appearance of crystals (Robiquet). — White, soft tufts of needles, having a silky lustre; also larger transparent prisms (Sertürner, Bucholz). Very bitter (Robinet). Neutral. Not altered by exposure to the air (Liebig). — When heated in a closed tube with alcohol to 200°, it blackens, forms a small quantity of ether recognisable by its odour, but no permanent gas (Reynoso, *Compt. rend.* 42, 686). — It dissolves in from 16 to 20 pts. cold water (Bucholz), in 20 pts. water at 18¾° (Abl; Cass & Garot), in less than 1 pt. boiling water (Merck). The aqueous solution does not deposit any morphine, even on repeated evaporation (Geiger). It is precipitated by concentrated hydrochloric acid (Hirzel). It dissolves in 40 parts alcohol (Cass & Garot), in 60 parts cold and in 10 parts hot alcohol of 80 p. c. (Wittstein). Insoluble in ether (Robinet). Dissolves in 19 parts of glycerin and in 800 parts of fat oil (Cass & Garot).

The crystals lose 14·23 p. c. water in a current of air at 130°, no more at 160° (Regnault), (6 at. = 14·38 p. c. HO).

			Dried.				Regnault.
34	C	....	204·0	....	63·45	....	63·45
	N	....	14·0	....	4·35	....	
20	H	....	20·0	....	6·22	....	6·42
6	O	....	48·0	....	14·93	....	
	Cl	....	35·5	....	11·05	....	10·64
C³⁴NH¹⁹O⁶,HCl		....	321·5	....	100·00	....	

Hydrofluate of Morphine. — Colourless, 'long, four-sided prisms. — Dissolves sparingly in water, not at all in alcohol or in ether (Elderhorst, *Ann. Pharm.* 74, 80; *Chem. Gaz.* 1850, 327).

Nitrate of Morphine. — Stellate rays (Sertürner), soluble in 1½ pts. of water (Choulant). The solution does not become coloured by continued boiling (Duflos).

An excess of *fluosilicic-alcohol* (xv. 437) forms a crystalline precipitate in solutions of morphine and its salts (Knop). — Morphine-salts are precipitated by *phosphotungstic acid* (a mixture of tungstate of soda and phosphoric acid), (Scheibler). *Phosphomolybdic acid* (xiii. 164) forms with them a pale-yellow flocculent precipitate (Sonnenschein). They are precipitated by *phosphantimonic acid* (xiv. 277), not, however, when diluted 1000 times (F. Schultze). *Chromate of potash* precipitates morphine from moderately dilute solutions (Neubauer, *Anal. Zeitschr.* 1, 516), J. André (*Zeitschr. Chem. Pharm.* 5, 651) did not obtain any chromate of morphine, on account of the rapid decomposition which took place. *Chloride of cadmium* forms, with hydrochlorate of morphine, double salts whose formulæ are, C³⁴NH¹⁹O⁶,HCl.7CdCl+4aq. and C³⁴NH¹⁹O⁶,HCl,2CdCl+5aq. (Gellatly, *N. Edinb. Phil. J.* 4, 94; *Chem. Centr.* 1856, 606). Kraut did not succeed in preparing these double salts.

Iodomercurate of potassium throws down from aqueous sulphate or hydrochlorate of morphine, a pulverulent precipitate, which soon becomes gelatinous, and is insoluble in hydrochloric acid (v. Planta, Delffs). When morphine, mercuric chloride, and iodide of potassium, are brought together in aqueous solution, a double-salt C³⁴NH¹⁹O⁶,Hg²I³,

[or $C^{34}NH^{19}O^6,HI,2HgI$? (Kr.)] is precipitated, sparingly soluble in water, more soluble in alcohol. With bromide of potassium, instead of the iodide, the corresponding bromine-compound is obtained. Both salts are crystallisable, free from water of crystallisation, not decomposible by dilute acids, even on boiling and on addition of iodide of potassium. They are decomposed by caustic alkalis (Groves, *Chem. Soc. Qu. J.* 11, 97; *Chem. Centr.* 1858, 890; *Kopp's Jahresber.* 1858, 363).

Chloromercurate of Morphine. — Mercuric chloride forms a white curdy precipitate with hydrochlorate of morphine (Caillot, *Ann. Chim. Phys.* 42, 263). With sulphate of morphine it forms, only after considerable concentration and addition of common salt, a milky (or pulverulent) precipitate, which afterwards changes to needle-shaped crystals (v. Planta). — On mixing aqueous hydrochlorate of morphine with mercuric chloride, the double salt is in part precipitated at once, the rest being gradually deposited in tufts of crystals; it is purified by recrystallisation from hot alcohol, and washing with cold water, alcohol, or ether. — Large, transparent, colourless crystals, having a glassy lustre; they may be obtained remarkably fine by leaving a solution in concentrated hydrochloric acid to evaporate over lime in vacuo. — Dissolves freely in cold concentrated hydrochloric acid, very little in cold water, alcohol, or ether, more freely in hot alcohol (Hinterberger, *Ann. Pharm.* 77, 205; *Wien. Akad. Ber.* 6, 104).

		Crystals.				Hinterberger. mean.
34	C	204·0	....	23·63	....	23·52
	N	14·0	....	1·62	....	
20	H	20·0	....	2·32	....	2·34
6	O	48·0	....	5·56	....	
4	Hg	400·0	....	46·32	....	46·12
5	Cl	177·5	....	20·55	....	
	$C^{34}NH^{19}O^6,HCl,4HgCl$	863·5	....	100·00	....	

Mercuric nitrate added to salts of morphine precipitates white flakes soluble in nitric acid (Duflos).

Chloroplatinate of Morphine. — Bichloride of platinum forms with hydrochlorate of morphine a yellow curdy precipitate, which when immersed in warm water, becomes soft, dissolves, and crystallises out on cooling (Liebig). Cold aqueous morphine is likewise precipitated by chloride of platinum after standing for some time.—The chloroplatinate dissolves in excess of morphine-salts and in acids (Duflos).

					Liebig.
$C^{34}NH^{19}O^6,HCl,Cl^2$....	391·5	....	79·87	....	
Pt	98·7	....	20·13	....	19·52
$C^{34}NH^{19}O^6,HCl,PtCl^2$	490·2	....	100·00	....	

Morphine-salts are not precipitated by *chloroiridiate of sodium* (v. Planta).

Formiate of Morphine. — Small bitter prisms, fusible, and easily soluble in water (Göbel).

Alcoholic *hydroferrocyanic acid* throws down from an alcoholic solution of morphine, after long standing, small white easily decomposible needles (Dollfus). — Aqueous *ferricyanide of potassium,* added to

an aqueous solution of hydrochlorate of morphine, forms after a while a crystalline, easily decomposible precipitate (Dollfus); according to Neubauer, on the other hand, it does not precipitate a solution of hydrochlorate of morphine, even when highly concentrated.

Cyanide of Platinum with Hydrocyanate of Morphine. — Cyanide of platinum and potassium throws down from the aqueous solution of acetate of morphine, an amorphous curdy precipitate which soon becomes crystalline, causing the liquid to solidify into a brilliant white mass. — Shining globules, and funnel-shaped depressed discs consisting of small microscopic needles, having a silky lustre when dry. The double salt becomes dark-yellow when heated and white again on cooling; melts partially at 150° to a brownish-yellow mass, and when further heated, swells up, gives off cyanogen, and burns with a sooty flame. — It does not give off any water of crystallisation at 125° (Schwartzenbach, *Pharm. Viertelj.* 8, 518; *Chem. Centr.* 1860, 304).

			Schwartzenbach.
			mean.
C³¹NH¹⁹O⁶,HCy,Cy	338·0	77·4	
Pt	98·7	22·6	22·63
C³⁴NH¹⁹O⁶,HCy,PtCy	436·7	100·0	

Hydrosulphocyanate of Morphine. — Sulphocyanide of potassium does not precipitate neutral salts of morphine (Artus, *J. pr. Chem.* 8, 253; Oppermann; Lepage, *J. Pharm.* 26, 140). It forms a light flocculent precipitate with acetate of morphine (O. Henry, *J. Pharm.* 24, 194); with the hydrochlorate and sulphate, a crystalline precipitate appearing at first like dust (v. Planta). — To prepare the salt, an alcoholic solution of morphine is saturated with hydrosulphocyanic acid not too dilute. — Small limpid shining needles. Melts at 100° (Dollfus, *Ann. Pharm.* 65, 214).

		at 90°.			Dollfus.
36	C	216	61·19		60·66
2	N	28	7·93		
21	H	21	5·95		5·80
7	O	56	15·86		
2	S	32	9·07		
	C³⁴NH¹⁹O⁶,C²NHS² + HO..	353	100·00		

Gerhardt (*Traité* 4, 36) regards the salt as anhydrous.

Acetate of Morphine. — A solution of morphine in excess of acetic acid is left to evaporate in the air (Geiger). Morphine is triturated with water; dilute acetic acid is slowly and cautiously added, till it dissolves no more of the morphine even after prolonged contact; and the filtrate is evaporated in shallow vessels between 38° and 50°, preferably in a current of air, since the salt is decomposed by gradual evaporation (Merck). By Kukle's method (*Baumgartner's Zeitschr. f. Phys.* 4, 182), which consists in dissolving morphine in alcoholic acetic acid and covering the solution with a large quantity of ether. a mixture of morphine and acetate of morphine is obtained, not completely soluble in ether (Merck, *Ann. Pharm.* 24, 46). — White silky needles grouped in tufts or cauliflower-like masses (Sertürner, Merck). Very bitter (Geiger). Neutral (Merck). When the solution is quickly evaporated, the salt remains as a colourless, transparent

varnish (Braconnot, Geiger).—The aqueous solution, when repeatedly evaporated by heat, loses a small portion of its acid, so that the residue is no longer completely soluble in water (Pelletier, *J. Pharm.* 9, 523, Geiger). The alcoholic solution mixed with a large quantity of ether, gives up to the ether a portion of the acid, so that morphine crystallises out (Merck).—Deliquescent (O. Henry, *J. Pharm.* 21, 226). Dissolves in 24 parts of water at $18\frac{3}{4}°$ (Abl, *Oesterr. pharm. Zeitschr.* 8, 201). Dissolves freely in water, less easily in alcohol (Buchholz), not at all in ether (Geiger). Soluble in 60 parts chlorcform (Schlimpert). — Contains 79·8 p. c. morphine; corresponding to the formula $C^{34}NH^{19}O^6,C^4H^4O^4 + 2Aq.$ (Calculation gives 79·2 p. c. $C^{34}NH^{19}O^6$) (Kieffer.)

Cyanurate of Morphine.—Tufts of long needles, mixed with crystals of cyanuric acid, even when morphine is present in excess. It is decomposed by recrystallisation, with formation of a white amorphous mass (Elderhorst, *Ann. Pharm.* 74, 84).

Mellitate of Morphine.—a. *Bibasic?* When cold aqueous mellitic acid is saturated with morphine and the solution evaporated, there remains a brown, amorphous, brittle mass (Karmrodt).

b. *Monobasic.*—The solution of morphine in hot concentrated aqueous mellitic acid soon deposits white, microscopic, needle-shaped crystals, which give off 2 p. c. of their weight at 110°. They are rather more soluble in cold than in hot water, freely in aqueous ammonia and potash, not in alcohol or in ether (Karmrodt, *Ann. Pharm.* 81, 171).

			Karmrodt. *mean.*
$C^{34}NH^{19}O^6,2HO$	303	75·94	
C^8O^6	96	24·06	24·90
$C^{34}NH^{19}O^6,C^8H^2O^8$	399	100·00	

Aspartate of Morphine.—Gum containing shining crystals. Very freely soluble in water (Plisson, *J. Pharm.* 15, 274).

Tartrate of Morphine.—a. *Neutral.*—When a solution of cream of tartar is neutralised with morphine, cream of tartar crystallises out first, then nodules of the morphine-salt, which must be removed in time, so as to keep them separate from the neutral tartrate of potash which afterwards crystallises out. The salt may be also obtained by slow evaporation of an aqueous solution of tartaric acid neutralised with morphine —Nodular groups of crystals consisting of closely aggregated needles. Effloresces on the surface at 20°; loses on the average 6·54 p. c. water at 130° ($2C^{34}NH^{19}O^6,C^8H^6O^{12} + Aq. = 6.76$ p. c. HO) no more at 145°. Exhibits crystal electricity (i. 319) when heated to 130° or 140°, and retains it for an hour after cooling.—Soluble in alcohol. The easily formed aqueous solution is not precipitated by caustic alkalis, alkaline carbonates, chloride of calcium, or ammonio-chloride of calcium (Arppe, *J. pr. Chem.* 53, 332).

b. *Acid.* The solution a. is mixed with as much tartaric acid as it already contains, and allowed to evaporate slowly.—Flat rectangular prisms which lose about 2 p. c. water below 140° ($C^{34}NH^{19}O^6,C^8H^6O^2 + Aq. = 1.98$ p. c. HO) caking together slightly at the same time and

becoming somewhat browned. In small quantities they are fusible without decomposition.—Less soluble in water than a. (Arppe).

Urate of Morphine. — Obtained by boiling uric acid and morphine with *water*. Crystallises on cooling from a solution saturated at the boiling heat, in short brownish prisms which decompose when re-crystallised (Elderhorst).

Croconate of Morphine. — Dark-yellow, uncrystallisable, bitter mass, soluble in water and in alcohol (Heller, *J. pr. Chem.* 12, 240).

Rhodizonate of Morphine. — Hyacinth-red; soluble, with reddish-yellow colour, in water and in alcohol (Heller).

Valerate of Morphine. Fine large hemihedral crystals belonging to the right prismatic system, with a fatty lustre on the faces. Smells strongly of valerianic acid. Rhombic prism (*Fig.* 53) having the obtuse lateral edge symmetrically truncated by p, the dome u resting on the acute lateral edges, and the octahedron x occurring only hemi-hedrally. $u : u$ above $= 125°\ 47'$, $x : y = 130°\ 0'$, $x : u = 148°\ 28'$; the acute lateral edges of y are sometimes bevelled by a prism of $102°\ 8'$ (Pasteur, *N. Ann. Chim. Phys.* 38, 445).

Pyrotartrate of Morphine. — Fissured gum, soluble in water and in alcohol (Arppe).

Picric acid forms with morphine-salts, a sulphur-yellow pulverulent precipitate (v. Planta); no precipitate with dilute acetate of morphine (Merck). Alcoholic picric acid does not precipitate alcoholic morphine (G. Kemp, *Repert.* 71, 164).

Hippurate of Morphine. — A hot saturated aqueous solution of hippuric acid does not yield any crystals after boiling with excess of morphine, but leaves on evaporation a syrup, which hardens to a transparent amorphous mass (Elderhorst).

Morphine-salts are not precipitated by *gallic acid* free from tannin (Pettenkofer, Pfaff).

Meconate of Morphine — Not crystallisable ; very soluble in water and in alcohol. — Reddens iron-salts (Robiquet, Liebig). It is present in the aqueous extract of opium.

Pectate of Morphine. — Recently precipitated pectic acid dissolves morphine even in the cold, forming a thick gum, which, after dilution with water, is thickened again by acids (Braconnot).

Kinate of Morphine. — Transparent gum exhibiting traces of crystallisation (Henry & Plisson, *J. Pharm.* 15, 406).

Tannate of Morphine. — Morphine-salts form a white precipitate with tincture of galls (Pettenkofer), and with tannic acid (Pelouze); even when diluted 900 times (O. Henry, *J. Pharm.* 21, 212). The precipitate is but sparingly soluble in water, freely in acetic acid, gallic acid (Pelouze), and mineral acids (Duflos). It is soluble in alcohol (Dublanc). If the morphine-salt contains free acid, no precipitate is formed ; sometimes even neutral hydrochlorate of morphine gives no precipitate until a trace of ammonia is added (Robiquet, *J. Pharm.* 25, 82). In dilute solutions of morphine-salts, a small quantity of tincture or infusion of galls produces a turbidity, which disappears on addition of a drop of hydrochloric acid, and reappears when more is added, if the tincture, and not the infusion of galls is used (v. Planta).

C. *With Alkalis.* Morphine dissolves in 117 parts of aqueous *ammonia* of sp. gr. 0·97 (Merck), remaining in crystals when the solution is evaporated (Duflos, Merck). Recently precipitated morphine dissolves in excess of carbonate and hydrochlorate of ammonia, but less freely than in pure ammonia (Riegel, Fresenius). Morphine or its acetate dissolves in an ammoniacal solution of oxide of copper, separating the hydrated oxide; since the compound of ammonia and morphine which is formed easily loses ammonia, the solution continually deposits morphine, which again precipitates hydrated oxide of copper (Kieffer).

Aqueous solutions of *potash* or *soda* dissolve morphine very freely, and deposit it in crystals when exposed to the air, in proportion as they absorb carbonic acid (Robinet, Wittstock). The solution may be precipitated by acetic acid (Braconnot), also by the alkaline bicarbonates, and by sal-ammoniac.

A solution of morphine in *baryta-water* when exposed to the air, deposits a mixture of morphine and carbonate of baryta (Robinet).— Warm *lime-water* dissolves morphine freely, forming a bitter liquid, which is precipitated by acids (Braconnot), and when exposed to the air, deposits morphine and carbonate of lime (Robinet).

D. *With Organic oxides.* — According to Choulant, morphine dissolves in 42 parts of cold or 36 parts of boiling *alcohol*; according to Buchholz & Brandes, in 24 parts boiling alcohol of 92 p. c. ; according to Merck, in 90 parts of cold alcohol of 96 p. c. : according to Pettenkofer, in 40 parts of cold or 30 parts of boiling absolute alcohol; according to Duflos, in 20 parts of cold, or 13·3 parts of boiling absolute alcohol. The solution in cold alcohol of 96 p. c. is not precipitated by water (Merck).

It is not soluble in cold or boiling *ether* (Duflos, Merck). Anhydrous ether dissolves a small quantity of morphine, but if shaken up with water, scarcely a trace; recently precipitated morphine dissolves in ether about three times as largely as the crystallised base (Petit). Ether containing alcohol dissolves morphine (Polstorf). From aqueous morphine (Petit), or from a solution of a salt of morphine supersaturated with carbonate or bicarbonate of soda, ether extracts the morphine, if shaken up with the liquid at once, but not if the morphine has been allowed to become crystalline. Ether does not extract morphine from solutions containing excess of potash or ammonia (A. Petit, *N. J. Pharm.* 43, 45). — Morphine is soluble in *acetic ether* (Valser, *N. J. Pharm.* 43. 49).

Morphine dissolves in 60 pts. *chloroform* (Schlimpert, *N. Jahrb. Pharm.* 13, 248), in 175 pts. (Pettenkofer, *N. Jahrb. Pharm.* 10, 270). — It is insoluble in *glycerin* (Cap and Garot, *N. J. Pharm.* 26, 81). — Very soluble in hot *fusel-oil* (J. Erdmann); insoluble in *benzol* (Rodgers, *Anal. Zeitschr.* 1, 516), and in *fixed oils* (Geiger; Cap & Garot).

Morphine is rendered more soluble in water by addition of *picrotoxine* (Pelletier & Couerbe, *Ann. Chim. Phys.* 54, 186). — See *Brucine.* — From its solution in acetic, sulphuric, or hydrochloric acid, not in excess, it is precipitated by 5 to 7 pts. *blood-charcoal*, or ignited bone-black (also from its alcoholic solution), but not by moist bone-black which has been purified by hydrochloric acid, and not re-ignited (Guthe). When a hydrochloric acid extract of opium is boiled with animal charcoal till all the morphine is precipitated, the washed and dried charcoal does not give up the morphine till boiled for some time with a very large quantity of alcohol (Bley, *N. Br. Arch.* 62, 162). The same observation was made by Lefort.

Conjugated Compounds of Morphine.

Sulphomorphide.

$$C^{34}NH^{18}SO^8 = C^{34}NH^{18}O^5,SO^3.$$
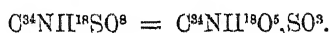
ARPPE. *Ann. Pharm.* 55, 96.
LAURENT & GERHARDT. *N. J. Pharm.* 14, 302; *N. Ann. Chim. Phys.*
24, 112; abstr. *Compt. rend.* 27, 80; *J. pr. Chem.* 45, 369; *Ann.*
Pharm. 68, 359.

Formation. By heating morphine with excess of sulphuric acid, or
by passing the vapour of anhydrous sulphuric acid over effloresced
morphine.

Preparation. Sulphate of morphine is evaporated down with a
slight excess of sulphuric acid, the heat being ultimately raised to 150°
or 160°; the brown residue is treated with water, which separates a
white substance; and the liquid is boiled till this substance is dissolved,
and then filtered hot. On cooling, it deposits sulphomorphide, a
further quantity of which may be obtained by boiling the yellowish
brown residue left on the filter, with addition of a little sulphuric acid.
It may be freed from adhering sulphuric acid by washing (Arppe).

Properties After drying it is whiter than before; if it has been too
strongly heated with sulphuric acid, it has a brownish colour. Non-
crystalline microscopic spherules (Arppe). Turns green, even when
kept in a sealed tube, also when heated to 130°—150° (Laurent &
Gerhardt).

				Arppe. *mean.*		Laurent & Gerhardt.
34 C	...	204	...	61·56	... 61·17	... 63·0
N	...	14	...	4·43	... 3·96	...
18 H	...	18	...	5·69	... 5·69	... 5·8
S	...	16	...	5·06	... 5·76	... 5·4
8 O	...	64	...	20·26	... 23·42	...
$C^{34}NH^{18}SO^8$	...	316	...	100·00	... 100·00	...

According to Arppe, it contains 4 at. morphine to 5 at. sulphuric acid. Laurent
& Gerhardt double the formula above given. — Differs from sulphate of morphine by
containing 2 at. less water, and is related thereto in the same manner as sulphate of
ammon (ii, 458) to sulphate of ammonia.

Decompositions. Sulphomorphide does not volatilise without de-
composition; when *heated* on platinum foil, it leaves a very bulky
cinder, difficult to burn (Laurent & Gerhardt). — 2. The solution in
hot water acquires an emerald-green colour by boiling. — 3. By con-
centrated *acids* or *alkalis*, it is decomposed, with formation of a brown
substance, but without reproduction of morphine (Arppe).

It appears to be slightly soluble in *water*. — In water containing
hydrochloric or *sulphuric acid* it dissolves very easily, without alteration
and without forming salts. The acid solutions yield copious precipi-

tates with ammonia, potash, and carbonate of ammonia; an excess of ammonia, but not of carbonate of ammonia, redissolves the precipitate, which turns green when exposed to the air. — From the solution in hydrochloric acid, baryta-salts throw down only part of the sulphur as sulphuric acid (Arppe).

Insoluble in *alcohol* and in *ether*.

Methyl-morphine.

$$C^{36}NH^{21}O^6 = C^{34}N(C^2H^3)H^{16}O^6,H^2.$$

H. How. *Chem. Soc. Qu. J.* 6, 125; *Ann. Pharm.* 88, 338.

Formemorphin.

Obtained as a hydriodate by heating finely pulverised morphine for half an hour to 100° in a sealed tube with absolute alcohol and iodide of methyl. The crystalline powder which separates on cooling, is collected and washed with alcohol, or crystallised from hot water.

From the warm aqueous solution of hydriodate of methyl-morphine, oxide of silver separates iodide of silver, forming *aqueous methyl-morphine*, which, when evaporated, leaves a brown translucent, amorphous mass. This mass is attacked by a mixture of iodide of methyl and alcohol, even in the cold, with formation of brown flocks, and at 100°, with formation of a brown resin, but without yielding a hydriodate of bimethyl-morphine.

Hydriodate of Methyl-morphine. — Colourless, shining, square prismatic needles which give off 4·15 p. c. water at 100° (2 at. = 4·04 HO). — Easily soluble in hot water.

		at 100°.				How.
36	C	216	....	50·57	....	50·47
	N	14	....	3·27	....	
22	H	22	....	5·15	....	5·36
6	O	48	....	11·26	....	
	I	127	....	29·75	....	29·66
$C^{34}N(C^2H^3)H^{18}O^6,HI$		427	....	100·00	....	

Ethyl-morphine.

$$C^{38}NH^{23}O^2 = C^{34}N(C^4H^5)H^{16}O^6,H^2.$$
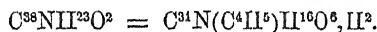
H. How. *Chem. Soc. Qu. J.* 6, 125; *Ann. Pharm.* 88, 336.

Vinemorphin.

Obtained as a hydriodate, by heating finely pulverised morphine with absolute alcohol and iodide of ethyl to 100° in a sealed tube for six hours. The crystals which separate on cooling are collected and washed with alcohol.

From the warm aqueous solution of hydriodate of ethyl-morphine, oxide of silver separates iodide of silver, forming *aqueous ethyl-morphine*. This solution assumes a dark brown colour as soon as the

hydriodate is completely decomposed; it is strongly caustic, and leaves, on evaporation, a solid, dark coloured, translucent residue, which does not crystallise.

Hydriodate of Ethyl-morphine separates, on cooling from solution in hot water, in slender white needles, which are permanent in the air, and give off 1·98 p. c. water (= 1 at.) at 100°. It is not decomposed by potash or ammonia. It dissolves easily in hot water and in weak spirit, but with difficulty in absolute alcohol.

			at 100°.			How.
38	C	.. ..	228	.. . .	51 71	.. 51·45
	N	. ..	14	. .. ..	3 17	....
24	H	..	24	..	5 11	. .... 5 74
6	O	.	48		10 87	
	I	.	127		28 81	28 50

$C^{34}N(C^4H^5)H^5O^6,HI$. 141   . .. 100 00   . ..

Appendix to Morphine.

1. Pseudomorphine.

PELLETIER. *J. Pharm.* 21, 575; *N. Br. Arch.* 5, 169; *Ann. Pharm.* 16, 49.

Discovered in 1835 by Pelletier & Thiboumery. — It was found, but only three times, in opium, the aqueous extract of which contained a large quantity of narcotine.

The morphine precipitated by ammonia from the aqueous infusion of opium, still contained narcotine in these cases, even after repeated crystallisation from alcohol; it was therefore dissolved in soda-ley, and filtered from the narcotine. After the alkaline solution had been acidulated with sulphuric acid, precipitated by ammonia, and separated from the precipitated morphine, it yielded, on concentration, whitish scales of pseudomorphine containing sulphuric acid, which were recrystallised from boiling water. After this treatment, they still retained 8·83 p. c. sulphuric acid, which could be extracted by boiling them with ammoniacal water.

Pseudomorphine containing sulphuric acid forms scales having a pearly lustre; when free from sulphuric acid, it forms dull scales. Cannot be melted or sublimed. Has no particular action on the animal organism.

Contains 51·7 p. c. C., 5·8 H., 4·08 N., and 38·42 O., agreeing with the formula $C^{27}NH^{18}O^{14}$ (Pelletier). See Couerbe's observations on this analysis (*J Pharm* 22, 25), and Pelletier's reply (*ibid.* 22, 31)

(It is not certain whether the following statements apply to pseudomorphine containing sulphuric acid, or free from it) — Pseudomorphine is decomposed by *heat*, even before melting. — By *dry* distillation it yields a small quantity of oil, a slightly acid watery distillate containing ammonia, and leaves a tumefied combustible cinder. *Nitric acid* colours pseudomorphine bright red, like morphine, and finally converts it into oxalic acid. — *Oil of vitriol* turns it brown, and decomposes it. — *Ferric salts* colour it bright blue, the colour disappearing on adding excess of any

acid (as with morphine). — Pseudomorphine likewise dissolves abundantly in a cold solution of ferric hydrochlorate, with blue colour, changing to dirty green when heated, and on subsequent addition of ammonia to wine-red, with separation of a slight precipitate.

Pseudomorphine containing sulphuric acid dissolves in 770 pts. water at 14°, in 12 pts. boiling water, and crystallises on cooling; when freed from sulphuric acid by ammonia, it becomes still less soluble. — Dilute acids, especially hydrochloric and acetic acid, facilitate the solution to a certain extent, whereas dilute nitric and sulphuric acid scarcely dissolve pseudomorphine.

Pseudomorphine is not perceptibly soluble in water containing *ammonia*, but dissolves readily in *potash-* and *soda-ley*, separating out again when the solution is neutralised.

In absolute *alcohol* and *ether* it is less soluble than in water; somewhat more in alcohol of 36°B.

2. Metamorphine.

WITTSTEIN. *Pharm. Viertelj.* 9, 481; *N. Br. Arch.* 105, 141; abstr. *Zeitschr. Chem. Pharm.* 4, 101.

Found in one instance in the residue of the preparation of opium-tincture, and obtained in the form of hydrochlorate in working up these residues for morphine by Couerbe's method. The hydrochlorate was decomposed with a quantity of sulphate of silver equivalent to that of the hydrochloric acid contained in it; the solution was filtered from the chloride of silver, and digested with carbonate of baryta; and the washed mixture of carbonate of baryta and metamorphine was treated with alcohol to extract the latter.

Properties. Flat hard prisms, $\frac{1}{17}$th of a line thick, united in stellate groups. It has no taste at first, but after a while exhibits a very faint, biting taste, not bitter. When slowly heated to 100°, it becomes dull, and at 130° assumes a grey-brown colour without melting, but when quickly heated it melts to a colourless liquid. The aqueous solution has no alkaline reaction; the alcoholic solution reacts slightly alkaline.

Decompositions. 1. Metamorphine, which has been fused by rapid heating, blackens quickly when further heated, and gives off an alkaline vapour. When slowly heated to 225°, it turns brown, but does not melt. — 2. *Oil of vitriol* dissolves metamorphine with faint transient coloration, the acid itself at the same time acquiring a grey-brown colour; oil of vitriol heated with hydrochlorate of metamorphine dissolves it with dirty red colour. — 3. Aqueous metamorphine colours *iodic acid* yellow, and slowly sets the iodine free. — 4. *Nitric acid* of sp. gr. 1·33 colours metamorphine orange-red, and dissolves it with yellow colour. — 5. *Ferric hydrochlorate* does not colour aqueous metamorphine, but imparts a greyish-blue colour to the hydrochlorate. — 6. *Nitrate of silver* produces a greyish-black turbidity in aqueous metamorphine. Hydrochlorate of metamorphine and

carbonate of silver yield chloride of silver; but instead of meta-morphine, a brown decomposition-product is obtained.

Combinations. Metamorphine dissolves in 6000 pts. of cold, and 70 pts. of boiling *water.*

It unites with acids, forming *salts.* — It dissolves quickly in *potash-ley,* more slowly in aqueous *ammonia;* also in aqueous carbonate of ammonia and carbonate of potash, especially when warmed. The same liquids dissolve the hydrochlorate.

Hydrochlorate of Metamorphine. — Slender white needles having a silky lustre; the aqueous solution is strongly and purely bitter. — Dissolves in 25 pts. cold, and 2 pts. boiling water; less freely in cold alcohol, and in 2 pts. boiling alcohol; insoluble in ether. — At 100° it gives off 11·56 p. c. water, and then contains 12·21 p. c. hydrochloric acid [therefore a larger proportion of hydrochloric acid than (air-dried) sex-hydrated hydrochlorate of morphine (Wittstein), but nearly as much as the morphine-salt dried at 100°, with which it is perhaps isomeric (Ludwig, *Apoth* k *Zeit* 1, 11)].

From hydrochlorate of metamorphine, *mercuric chloride* throws down white flocks; from *terchloride of gold,* reddish-yellow; from *bichloride of platinum,* light yellow flocks soluble in water. *Tannic acid* produces in the solution a yellowish-white turbidity.

Metamorphine dissolves in 330 pts. of cold, and 9 pts. of boiling *alcohol* of 90 per cent. It is insoluble in *ether.*

3. Porphyroxine.

E. MERCK. *Ann. Pharm.* 21, 201.

Occurs to the amount of ½ per cent. in East Indian, also in Smyrna opium, and probably also in other sorts ; not in the alcoholic extracts of European poppy-heads. — On Gibb's porphyroxine, see the appendix to *Chelerythrine.*

On the relation of porphyroxine to acids, Haussler (*N. J. Pharm.* 14, 187) founds a process for the detection of opium. See also Robertson (*N. J. Pharm.* 22, 190 ; *Lieb. Kopp's Jahresber.* 1852, 712).

Preparation. When opium is exhausted with boiling ether, the residue heated with water and a small quantity of carbonate of potash, and then again treated with boiling ether, the ether takes up codeine, thebaine, porphyroxine, and caoutchouc, which remain behind when the solution is left to evaporate. The residue is dissolved in cold, very dilute hydrochloric acid, and the solution is filtered and precipitated by ammonia ; whereupon codeine remains dissolved, while thebaine and porphyroxine are precipitated. On dissolving the dried and pulverised precipitate in boiling ether, and leaving the solution to evaporate in the air, crystals of thebaine and resinous porphyroxine remain behind, and may be separated by alcohol, which easily dissolves the porphyroxine.

Properties. Slender, shining needles. Neutral.
With *oil of vitriol,* and with *nitro-sulphuric acid,* it assumes an olive-

green colour. The colourless solution in dilute *sulphuric, hydrochloric,* or *nitric acid* assumes, on boiling, a purple-red colour, changing to rose-red on dilution; the solution in *acetic acid* remains colourless, even at the boiling heat. Alkalis decolorise the liquids, and produce a white precipitate; and on subsequently adding any acid, even acetic acid, to the solution, the red colour is restored without the application of heat. The purple-red solution in hydrochloric acid is precipitated by protochloride of tin and by tannic acid; neutral acetate of lead renders it rose-red; chloride of gold, dirty red; it is not precipitated by sulphate of copper. Ferrous hydrochlorate colours the solution brown.

Insoluble in *water* (Riegel).

Porphyroxine is precipitated by alkalis from its colourless solution in dilute acids, as a loose bulky mass, which cakes together when heated, and is very friable when cooled (Merck). It dissolves slowly in concentrated aqueous tartaric acid, and on mixing the solution with bicarbonate of soda, the porphyroxine is thrown down as a dirty white precipitate insoluble in excess of the precipitant (Riegel, *N. Br. Arch.* 58, 288). — Porphyroxine is easily soluble in *alcohol* and in *ether.*

Primary Nucleus $C^{34}H^{26}$; *Oxygen-nucleus* $C^{34}H^{16}O^{10}$.

Evernic Acid.

$$C^{34}H^{16}O^{14} = C^{34}H^{16}O^{10}, O^4.$$
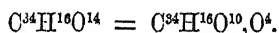
STENHOUSE. *Phil. Trans.* 1848, 79; *Ann. Pharm.* 68, 83; abstr. *N. J. Pharm.* 15, 229.

O. HESSE. *Ann. Pharm.* 117, 297.

Occurrence. In *Evernia prunastri,* according to Stenhouse, together with usnic acid; according to Hesse, in variable and sometimes very small quantity. Rochleder & Heldt, who found lecanoric acid (xii. 337) in *Ev. prunastri,* appear to have examined another lichen (Stenhouse).

Preparation. The extract of the lichen, prepared with thin milk of lime (as in the preparation of lecanoric acid, xii. 337, 3), is precipitated with hydrochloric acid, and the precipitate is either boiled with dilute alcohol, or dried and exhausted with ether. The evernic acid, which passes into the solution, must be purified by recrystallisation, with help of animal charcoal. — Stenhouse treats the precipitate produced by hydrochloric acid, with alcohol, only till ⅔rds of it is dissolved; the usnic acid is then left behind.

Properties. Colourless needles, without taste or odour, having an acid reaction, and not giving off any water at 100° (Stenhouse). White crystals arranged in spherical groups, melting at about 164° (Hesse).

	Over oil of vitriol, or at 100°.		Stenhouse. *mean.*	Hesse.
34 C	204	.... 61·44	...... 61·62	.... 61·5
16 H	16	.... 4·82	.... 5·08	... ... 5·2
14 O	112	.... 33·74	.... 33·30	.... 33·3
$C^{34}H^{16}O^{14}$	332	...... 100·00	... . 100·00	.... 100·0

Decompositions. 1. Evernic acid heated on platinum-foil *burns* easily and without residue. — 2. By *dry distillation* it yields an empyreumatic oil and a sublimate of orcin (Stenhouse). — 3. The acid absorbs *bromine* (Hesse). — 4. Aqueous *chloride of lime* colours it yellowish. — 5. The solution in excess of *ammonia* acquires a dark-red colour by exposure to the air for a few days. — 6. When a solution of evernic acid in a slight excess of *potash-ley* or *baryta-water* is boiled for a few minutes, everninic acid, orcin, and carbonic acid are produced (Stenhouse):

$$C^{34}H^{16}O^{14} + 2HO = C^{18}H^{10}O^3 + C^{14}H^4O^4 + 2CO^2:$$
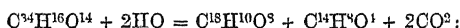
but it is possible that orsellic acid (xii, 371) may be produced, together with everninic acid, in the first instance, and afterwards resolved into carbonic acid and orcin (Strecker, *Ann. Pharm.* 68, 112).

Combinations. Evernic acid is insoluble in cold, sparingly soluble in boiling *water*, and separates in white flakes on cooling (Stenhouse).

Potash-salt. The solution of evernic acid in excess of cold potash-ley, solidifies to a crystalline pulp when carbonic acid is passed through it, the potash-salt being easily soluble in potash-ley, but not in cold water or in carbonate of potash. The crystals are purified by recrystallisation from weak spirit, with help of animal charcoal. Colourless, and with a fine silky lustre (Stenhouse).

	Crystals.		Stenhouse. *mean.*
34 C	204	.... 55·14	.... 55·55
15 H	15	.... 4·06	.... 4·35
13 O	104	.... 28·10	.... 27·80
KO	47	.... 12·70	.... 12·30
$C^{34}H^{15}KO^{14}$	370	.... 100·00	.... 100·00

Baryta-salt. — The acid is triturated with baryta-water; carbonic acid is passed into the mixture; and the precipitate is treated with warm dilute alcohol, which takes up the salt and deposits it on evaporation in small groups of heavy crystals. — Dissolves slightly in water, very easily in weak spirit (Stenhouse, Hesse).

	at 100°.		Stenhouse. *mean.*
34 C	204·0	.... 49·95	.... 50·31
16 H	16·0	.... 3·91	.... 4·03
14 O	112·0	.... 27·48	.... 27·23
BaO................	76·4	.... 18·66	.... 18·43
$C^{34}H^{15}BaO^{14} + Aq$	408·4	.... 100·00	.... 100·00

It appears then to retain 1 at. water at 100° (Stenhouse, Hesse). The latter found 18·65 p. c. baryta.

The acid dissolves in cold *alcohol*, very abundantly in hot alcohol, and easily in *ether*.

Appendix to vol. xiii. p. 355.

1. Everninic Acid.

$$C^{18}H^{10}O^8 = C^{18}H^{10}O^4,O^4$$
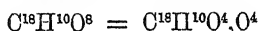
STENHOUSE. *Ann. Pharm.* 68, 86.
HESSE. *Ann. Pharm.* 117, 299.

Formation. By boiling evernic acid with strong bases (p. 444).

Preparation. Evernic acid is boiled for a short time with a slight excess of baryta-water; the solution is filtered from carbonate of baryta; and the resulting everninic acid is precipitated by hydrochloric acid, and purified by recrystallisation, with help of animal charcoal. The orcin remains in the filtrate (Stenhouse). If the lichen is rich in evernic acid, it may be boiled with water, the slightly acid distillate concentrated to a considerable extent, and mixed after removal of the separated brown substances, with hydrochloric acid, whereupon the liquid, which is milky at first, becomes clear after standing for some time, from separation of crystalline everninic acid. This product must be recrystallised from boiling dilute alcohol and decolorised with animal charcoal, after neutralisation with ammonia; the ammonia-salt is then decomposed by hydrochloric acid (Hesse).

Properties. Long capillary needles having a silky lustre (Stenhouse). Crystals resembling benzoic acid, and melting at 157° (Hesse), giving off at high temperatures a suffocating vapour and a colourless sublimate (of unaltered acid? Kr.) (Stenhouse, Hesse). Tasteless and inodorous (Stenhouse), tastes slightly acid (Hesse). Reddens litmus. Does not lose weight at 100°.

	Crystals.			Stenhouse.	Hesse. *mean.*
18 C	108		59·34	59·37	58·9
10 H	10		5·49	5·72	5·6
8 O	64		35·17	34·91	35·5
$C^{18}H^{10}O^8$	182		100·00	100·00	100·0

Differs from orsellic acid (xii, 371) and from carbohydrokinonic acid (xvi. 235) by C^2H^2 and C^4H^4 respectively, but is not homologous with these acids (Hesse). Isomeric with veratric acid (xiii. 354).

It is scarcely attacked by cold dilute *nitric acid;* the concentrated acid attacks it when heated, giving off red fumes. The products of the reaction are evernitic and oxalic acids (Hesse). — It dissolves in *oil of vitriol,* the solution becoming brown after a while; it dissolves with brown colour in fuming sulphuric acid, and becomes carbonised when heated, with evolution of sulphurous acid (Hesse). The

ammoniacal solution does not turn red on exposure to the air. — With *chloride of lime* it assumes a yellowish colour. — When boiled with *potash-ley* or *baryta-water*, it does not yield orcin (Stenhouse). — Aqueous everninic acid is coloured violet by *ferric hydrochlorate* (Hesse).

Nearly insoluble in cold, easily soluble in boiling *water*.

Everninate of Potash. — Crystalline laminæ, very easily soluble in water and hot alcohol, sparingly in cold weak spirit (Stenhouse).

Baryta-salt. — Evernic acid is boiled with a slight excess of baryta-water; the solution is neutralised by passing carbonic acid through it, then filtered and evaporated; and the residue is freed from orcin and colouring matter by washing with ether or cold alcohol. The undissolved baryta-salt may be crystallised from warm weak spirit. — Hard, four-sided prisms, containing, after two days' drying in a vacuum, 2 at. water, and after four days, 1 at., which it gives off at 100°.

Anhydrous.			*With* 1 *at. water.*			*With* 2 *at water.*		
18 C	108·0	43·30	18 C	108·0	41·79	18 C	108·0	40·38
9 H	9·0	3·61	10 H	10·0	3·87	11 H	11·0	4·11
7 O	56·0	22·46	8 O	64·0	24·82	9 O	72·0	26·94
BaO	76·4	30·63	BaO	76·4	29·52	BaO	76·4	
	249·4	100·00		158·4	100·00		277·4	100·00

Analyses by Stenhouse.

	at 100°.	*4 days in vacuo.*	*2 days in vacuo.*
C	43·13	42·12	41·11
H	3·91	4·24	4·28
O	22·80	24·36	26·11
BaO	30·16	29·28	28·20
	100·00	100·00	100·00

Silver-salt. Obtained as a white precipitate by treating the ammonia-salt with nitrate of silver (Stenhouse).

				Stenhouse.
18 C	108	37·37	37·12
9 H	9	3·12	3·22
7 O	56	19·38	19·66
AgO	116	40·13	40·00
	289	100·00	100·00

Everninic acid is readily soluble in hot *alcohol.* It dissolves in *ether* (Stenhouse), less easily in boiling *benzene.*

2. Everninate of Ethyl.

$$C^{22}H^{14}O^8 = C^4H^5O,C^{18}H^9O^7.$$
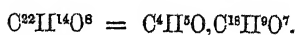
Stenhouse. *Ann. Pharm.* 68, 90.

Everninic acid.

When evernic acid is boiled for a short time with strong alcohol and hydrate of potash till it is dissolved, carbonic acid gas then passed into the brown liquid, and this liquid concentrated and left to cool, long prisms are obtained, while orcin remains in the mother-liquor. — The same crystals are produced on boiling evernic acid with absolute alcohol for 8 or 10 hours, and may be obtained, though contaminated with resin, by evaporating the solution to dryness, and extracting the orcin with cold water. They are not formed on passing hydrochloric acid gas into an alcoholic solution of everninic acid, which therefore appears to produce the ethylic ether only when in the nascent state.

Long white prisms, which melt at 56°, and solidify in the crystalline form on cooling. Tasteless and inodorous.

				Stenhouse.		
						mean.
22 C	....	132	....	62·86	....	62·93
14 H	....	14	....	6·67	.....	6·94
8 O	.. ..	64	....	30·47	.	30·13
$C^4H^5O, C^{18}H^9O^7$		210	....	100·00	....	100·00

Stenhouse, by treating the ether with melting hydrate of potash, obtained alcohol but no orcin; hence the compound cannot be the ether of evernic acid.

Not altered by boiling *hydrochloric acid*, or coloured by solution of *chloride of lime.* — The alcoholic solution is not altered by boiling with *potash-ley.*

Nearly insoluble in cold, very sparingly soluble in boiling *water;* insoluble in aqueous *ammonia* and *carbonate of potash*, but easily soluble in *potash-ley*, and precipitated in its original state by hydrochloric acid. — Its solutions are not precipitated by *basic acetate of lead.*

Easily soluble in *alcohol* and in *ether.*

3. Evernitic Acid.

$$? \ C^{18}N^3H^9O^{16} = C^{18}X^3H^9, O^4.$$
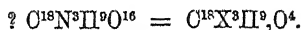
HESSE. *Ann. Pharm.* 117, 300.

Everninic acid is heated with 10 times its weight of pure concentrated nitric acid till it is dissolved, with evolution of nitrous gas; the solution is neutralised with carbonate of soda, and evaporated to dryness; and the residue is boiled with alcohol. The solution, after being freed from the greater part of the alcohol by distillation, and then left to cool, deposits a small quantity of amorphous substance which must be removed; and the filtrate, if then treated with nitric acid, yields evernitic acid.

Capillary, pale yellow prisms, often several inches long, or white crystalline powder. Has an acid reaction in alcoholic, but not in aqueous solution. Melts when heated, and then carbonises; when quickly heated it detonates slightly.

Dissolves in 830—1000 pts. *water* at 25°, more easily in boiling

water, forming a yellow solution, which has a bitter taste, colours the skin yellow, and becomes turbid on cooling, from separation of oil-drops, which afterwards change to crystals.

Soluble in *nitric acid.*

Potash-salt. — When carbonic acid is passed through a solution of evernitic acid in aqueous potash, the greater part of the potash-salt separates out, and may be washed with water and dried in the air. — Neutral, orange-red needles, which detonate when heated, and are carbonised by oil of vitriol. It dissolves with yellow colour in water and in alcohol. — Over oil of vitriol it gives off 6·7 p. c. water (3 at. = 6·76 p. c.).

		Over oil of vitriol.			Hesse.
18	C	108·0	29·00	28·6
3	N	42·0	11·28	
8	H	8·0	2·12	2·8
17	O	136·0	36·55	
2	K	78·4	21·05	21·7
	C¹⁸X³K²H⁷O⁴ + aq	372·4	100·00	

Hesse likewise regards as possible, the formula C¹⁸K²H²H⁶O⁸ + 3aq., which requires nearly the same numbers.

Baryta-salt. — Brownish yellow needles, which separate after a while from the solution of the soda-salt mixed with acetic acid and acetate of baryta. — Detonates with great violence and leaves charcoal.

Lead-salt. — Neutral acetate of lead added to the solution of an evernitate mixed with acetic or nitric acid, throws down stellate groups of brown-yellow needles, which detonate when heated, and after drying at 100° contain 30 p. c. lead. — Neutral or basic solutions yield lead-salts of different composition.

Evernitic acid dissolves easily in *alcohol;* it is likewise soluble in *ether.*

Primary Nucleus C³⁴H²⁸; *Oxyazo-nucleus* C³⁴NH²¹O⁶.

Atropine.

$$C^{34}NH^{23}O^6 = C^{34}NH^{21}O^6,H^2.$$
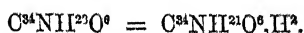
GEIGER & HESSE.   *Ann. Pharm.* 5, 43 and 6, 44; further, 7, 269 and 272.

LIEBIG.   *Ann. Pharm.* 6, 66.

MEIN.   *Ann. Pharm.* 6, 67.

O. HENRY.   *J. Pharm.* 21, 226.

BRANDES.   *Ann. Pharm.* 9, 122.

H. TROMMSDORFF.   *N. Br. Arch.* 18, 82.

W. RICHTER.   *J. pr. Chem.* 11, 29; abstr. *Ann. Pharm.* 24, 212.

v. PLANTA.   *Ann. Pharm.* 74, 245; *Pharm. Centr.* 1850, 561; *Chem. Gaz.* 1850, 349; *Lieb. Kopp's Jahresber.* 1850, 433.

HINTERBERGER.   *Wien. Akad. Ber.* 7, 432; *Ann. Pharm.* 82, 318.

H. LUDWIG.   *N. Br. Arch.* 107, 129.

W. ORMLEY.   *Chem. News.* 2, 13; *Rep. Chim. pure* 2, 429.

Daturine. Discovered in 1831 by Mein, and in 1833 by Geiger & Hesse, the latter of whom showed that the products previously described as atropine, especially the volatile atropine of Brandes (*Ann. Pharm.* 1, 68 and 230) were not the active principle of belladonna, and moreover were not pure. Liebig & v. Planta established the composition of atropine, and the latter demonstrated its identity with daturine.

Occurrence. In the Deadly Nightshade (*Atropa Belladonna*) and the Thorn-apple (*Datura Stramonium*). — In the seed of *Datura arborea* (Walz, *Jahresb. pr. Pharm.* 24, 353).

Richter's *atropic acid* from belladonna-roots forms long spicular crystals, volatile, different from benzoic acid; it has not yet been satisfactorily investigated (*J. pr. Chem.* 11, 33).

Commercial atropine contains, according to Hübschmann (*Schweiz. Pharm. Zeitschr.* 1858, No. 5; *Pharm. Viertelj.* 8, 126; *N. Br. Arch.* 90, 62), a second base, Hübschmann's *belladonnine*, which, when a salt of atropine is imperfectly precipitated by carbonate of potash, separates first as a liquid resin. It forms a nearly colourless, amorphous gum, having a slightly bitter, burning, sharp taste, and alkaline reaction. It is but slightly soluble in water, neutralises acids, and is precipitated from its sulphate by ammonia. Its solution in dilute alcohol forms a white precipitate with tartar-emetic, orange-coloured with bichloride of platinum, grey with nitrate of silver, reddish yellow with chloride of gold; no precipitate with basic acetate of lead or sulphocyanide of potassium. Sulphate of belladonnine forms a white precipitate with tannic acid. Belladonnine is soluble in alcohol and in ether. It is perhaps amorphous atropine? (Kr.) — (On Lubeking's belladonnine, see *N. Br. Arch.* 18, 75, and *Berzel. Jahresber.* 20, 325).

Preparation. From the herb of Deadly Nightshade. 1. The fresh plant, gathered immediately before flowering, is bruised; the juice is expressed, heated to 80° or 90°, till the albumin coagulates, then filtered and left to cool; and caustic potash and chloroform are added to it in the proportion of 4 grms. potash and 30 grms. chloroform to a litre. The liquid having been agitated and left at rest for half an hour, the chloroform, holding atropine in solution, settles down to the bottom as a greenish oil, which is collected, washed with water, and distilled. The residue is dissolved in water acidulated with sulphuric acid; the liquid filtered; the filtrate mixed with carbonate of potash; and the precipitated atropine is collected and purified by recrystallisation from alcohol. (Rabourdin, *N. J. Pharm.* 18, 407; *J. pr. Chem.* 51, 256). Atropine may also be prepared from *Extractum Belladonnæ* (Rabourdin).

2. Extract of belladonna is dissolved in water, and the solution filtered, mixed with excess of caustic soda and agitated with ether, which must be pipetted off after a while and renewed. The first ethereal extract, when evaporated, leaves yellowish, the second greenish atropine; the extract, after having been twice treated with ether, still yields to ether-alcohol a certain quantity of atropine, but more impure; it may be purified by solution in sulphuric acid, separation with soda-ley, and solution in ether. — As the whole of the atropine thus obtained still contains chlorophyll and fat, its solution in a slight excess of dilute sulphuric acid is digested with animal charcoal till it becomes pale yellow, then filtered and precipitated with soda-ley; and the precipitate, when it no longer increases, is collected, washed, pressed, dried, and crystallised from boiling water (Geiger & Hesse).

From the roots of Deadly Nightshade. — 1. The freshly pulverised roots are exhausted by several days' digestion with alcohol; the tinc-

tures are agitated with a quantity of dry hydrate of potash equal to $\frac{1}{3\frac{1}{2}}$th of the weight of roots employed, then filtered, neutralised with dilute sulphuric acid, and freed from separated gypsum by filtration, and from alcohol by distillation ; and the residue, when it amounts to twice the weight of the roots employed, is mixed by drops with a strong solution of carbonate of potash, till the liquid exhibits a dirty turbidity. On standing, it deposits a resin, which is filtered off after some hours ; and the filtrate, mixed with carbonate of potash, and left to itself for 12 or 14 hours, yields crystallised atropine. The atropine thus obtained is collected, pressed, dried, stirred up with water, again pressed and dried, and dissolved in alcohol; the alcoholic solution is poured into water ; and the liquid is left to itself and concentrated, if necessary, till it deposits crystals, which are purified by recrystallisation (Mein). — 2. Procter (*Kühtze's Notizen*, 13, 13), drenches and exhausts the pulverised roots with alcohol in a percolator; agitates the tincture with slaked lime ; leaves it in contact therewith for 24 hours ; slightly supersaturates the decanted liquid with sulphuric acid ; then filters and evaporates it to a syrup ; removes the fat which separates; dilutes ; filters ; agitates the filtrate with chloroform (which does not dissolve sulphate of atropine) ; removes the chloroform ; adds potash-ley in sufficient quantity to produce an alkaline reaction ; then fresh chloroform, which now takes up the atropine, and after being separated from the rest of the liquid, leaves it behind on evaporation. The atropine thus obtained is purified by recrystallisation, with help of animal charcoal.

3. Eight pounds of belladonna-roots are exhausted with cold water; the infusion is brought into a state of fermentation by addition of yeast at 20° or 30°, in order to destroy the sugar; the fermented liquid is filtered and boiled up; the filtrate is evaporated to a syrup, and this syrup is mixed with 8 oz. of aqueous ammonia and 4lbs. of alcohol. The tincture decanted after 24 hours is distilled; and the residue is evaporated over the water-bath to an extract, which is shaken up with 2 oz. of ammonia and 1lb. of alcohol, and afterwards with 1lb. of ether. The limpid liquid separated from the deposit is distilled, and the residue mixed with water is evaporated to a syrup and stirred up with concentrated ammonia, which throws down the whole of the atropine as a yellow-brown precipitate, while Richter's atropic acid (p. 449) and other substances remain in solution. The precipitate is washed with ammonia-water; melted in the water-bath under a small quantity of water ; warmed with 16 pts. water; neutralised with dilute sulphuric acid; and heated to boiling with animal charcoal. The filtrate, evaporated to the crystallising point and immediately mixed with ammonia, deposits white atropine, which must be washed with ammonia, and freed from ammonia by fusion under a small quantity of water (W. Richter).

Bouchardat (*Lieb. Kopp's Jahresber.* 1849, 387; *Gerhardt's Traité*, 4, 201), precipitates the atropine from its aqueous solution by biniodide of potassium; decomposes the precipitates with zinc and water; and after decomposing the iodide of zinc with carbonate of potash, extracts the atropine with alcohol.— Comp. Henry's method, vii, 177, 3; also the process of Samuel Sinnes (*J. Pharm.* 20, 201).— Luxton's process (*Pharm. J. Trans.* 14, 299), yields no atropine, but o ly ammonio-magnesian phosphate. F. Muck (*Pharm. Viertelj.* 5, 219).— Weppen (. *Br. Arch.* 87, 152).

When thorn-apple seeds are used for the preparation of atropine,

the product must be boiled for a considerable time with alcohol. — Whatever method may be adopted for the preparation of atropine, boiling or prolonged contact with caustic alkalis or magnesia must be avoided (Geiger & Hesse ; Brandes). — The yield does not exceed ⅓ p. c. of the dried belladonna-root (from the herb of belladonna, and from thorn-apple seeds it is even less) (Procter). — On the detection of atropine in the urine of persons who have been poisoned with it, see Allan (*Ann. Pharm.* 71, 233) ; also Bley (*N. Br. Arch.* 91, 1).

Properties. Colourless, shining prisms and needles grouped in tufts ; from alcohol it is obtained, partly in crystals, partly as a vitreous mass which becomes crystalline after some time only (Geiger & Hesse). It melts at 90°, without loss of weight, to a transparent mass which becomes brittle on cooling, exhibits stellate groups of needles when further heated and cooled, and volatilises partially without decomposition at 140° (v. Planta ; Geiger & Hesse). On heating it between two watch-glasses, part of it sublimes, condensing in the form of varnish (Mein), in indistinct crystals (Richter). By prolonged boiling with water, a small portion of it is volatilised (Geiger & Hesse). — Heavier than water. Inodorous in the pure state, but has an offensive odour when impure. Has a very repulsive bitter taste, with long-continued after-taste. Acts as a narcotic poison, and dilates the pupil when introduced into the eye (Geiger & Hesse ; Mein). On the action of atropine, see Schroff (*N. Repert.* 5, 503) ; Czermak (*Wien. Akad. Ber.* 39, 132 and 526). After poisoning with stramonium, atropine is found in the urine (Allan). — Permanent in the air. Exerts an alkaline reaction on litmus and turmeric (Geiger & Hesse ; Mein). Exhibits slight lævorotatory power (Buignet, *Compt. rend.* 52, 1085).

| | | | | Liebig. | | v. Platna. | |
				a.	*mean.*	*b.*	
34	C	....	204	.... 70·58	.... 70·03	.... 70 23	.... 69·30
	N	....	14	.... 4·85	.... 4·83	.... 5·26	.... 4·94
23	H	....	23	... 7·96	.... 7·83	... 8·23	.... 8·01
6	O	....	48	.... 16·61	. 17·31	... 16·28	.... 17·75
$C^{34}NH^{23}O^6$ ..		289	.... 100·00	.. 100·00	.... 100·00	.... 100·00

a obtained from *Atropa ;* *b* from *Datura.*

Decomposition. 1. When heated for some time to 100°, it turns brown without further decomposition, and between 150° and 190° becomes darker, and partly volatilises. At a stronger heat, a small quantity of water and oily liquid passes over, which is very poisonous, then a thick brown empyreumatic oil, together with ammoniacal vapours, while charcoal remains behind (Geiger and Hesse.) — 2. When heated in contact with the *air*, it swells up, emits offensive white vapours, *burns* with a bright very fuliginous flame, and leaves a shining black charcoal, which disappears on continued ignition (Geiger & Hesse ; Mein). The vapour of burning atropine smells like benzoic acid (Ludwig).—3. By prolonged contact with *water* and air, either at ordinary or at higher temperatures, it becomes uncrystallisable, yellow, fetid, soluble in all proportions in water, but is not completely decomposed (Geiger & Hesse). — 4. In *chlorine gas* it assumes a pale yellow colour, melts, and is converted into hydrochlorate of atropine, without further alteration (Geiger & Hesse). — 5. Strong *nitric acid* dissolves

atropine with pale-yellow colour, changing to orange when heated, the liquid at the same time giving off a small quantity of nitrous fumes and becoming colourless and transparent when boiled. It does not contain nitric acid, still exhibits the reactions of atropine with tincture of iodine and tincture of galls, but exerts scarcely any action on the pupil of the eye (Geiger & Hesse). — 6. Aqueous *chromate of potash* is reduced by atropine only after addition of dilute sulphuric acid; on boiling and concentrating the green solution, benzoic acid is evolved, and the residue, if then treated with potash, gives off alkaline vapours smelling like herrings:

$$C^{31}NH^{23}O^6 = C^{14}H^4O^2 + C^{14}H^6O^4 + C^6NH^9 \text{ (H. Ludwig).}$$

Benzylic   Benzoic   Propyl-
alcohol.   acid.   amine.
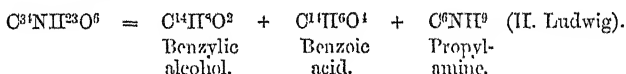
According to Pfeiffer, however (*Ann. Pharm.* 128, 275), the only nitrogenous compound formed in the reaction is ammonia. See also decomposition with baryta. — 7. *Oil of vitriol* dissolves atropine in the cold without colour, the solution when heated becoming red, then black, and giving off sulphurous acid (Geiger & Hesse). The colourless solution of atropine in cold oil of vitriol turns brown when heated (Mein; Guy), and gives off the odour of orange-flowers (Gulielmo, *Pharm. Viertelj.* 12, 219). — 8. When a dilute solution of sulphate of atropine containing excess of *acid*, is exposed to a heat of 100°, the atropine is resolved into ammonia, and a brown resinous mass, which is insoluble in water but soluble in alcohol and ether, has no alkaline reaction, but dissolves in aqueous acids, forming solutions which exhibit a blue fluorescence when mixed with excess of ammonia (Geiger & Hesse). Atropine when boiled with dilute acids, does not yield any sugar (Ludwig).

9. Aqueous *alkalis* decompose atropine but slowly in the cold, and only after 24 hours' contact, but on heating the liquid, complete decomposition takes place, attended with evolution of ammonia and formation of brown products (Geiger & Hesse). Atropine boiled with strong potashley, melts to drops of oil, which float on the alkaline liquid in that form long after cooling (Ludwig). Ammonia and oxide of silver do not act upon atropine, even with the aid of heat (Geiger & Hesse).

¶ Atropine heated with 6 pts. of hydrate of soda dissolved in 15 pts. water, is resolved into a *volatile base* and an *acid*, the soda-salt of which, when freed from excess of soda, and purified by solution in absolute alcohol, addition of ether (which precipitates admixed soda-salts), and evaporation of the filtrate, forms a clear varnish-like mass, which cannot be made to crystallise even at 0°. Its aqueous solution is slightly alkaline. It dissolves completely in a small quantity of water, but the solution becomes turbid on addition of a larger quantity. On evaporating the filtered solution, redissolving in water, and adding hydrochloric acid, the organic acid separates in oily drops which afterwards crystallise. It may be freed from chloride of sodium by washing with cold water, in which it is but slightly soluble, then dissolved in the smallest possible quantity of hot water, and freed by filtration from a small quantity of an acid resinous substance, which appears to be a product of its decomposition. From the hot filtered solution it is deposited on cooling in rhombic tables resembling benzoic acid. It melts at about 98°, solidifies at about 95°, and at 105° begins to sublime without decomposition in white needles. Its vapour is pungent like that of benzoic acid, but has more of a sweetish character. When it is oxidised with bichromate of potash and sulphuric acid, the pungent odour of benzoic acid becomes more decided. The acid, purified as completely as possible and perfectly white, gave by analysis 73·6 p. c. carbon and 6·1 hydrogen, whence Pfeiffer assigns to it the formula C^{20}H^{10}O^4 (calc. 74·1 C. and 6·2 H.), but it ...es almost as nearly with Kraut's atropic acid C^{18}H^{8}O^1 (p. 458). — The *volatile* ... forms a hydrochlorate which crystallises in splendid concentric groups of needles

shooting out in arborescent forms at the edges, and deliquescing in the air. Two grms. atropine yielded 1·65 grm. of the soda-salt above described, and only 0·30 grm. of the hydrochlorate of this base. — An analysis of the hydrochlorate, made with a very small quantity (0·1 grm.) gave 51·4 p.c. C., 10·0 H., 20·7 Cl and 10·1 N., leaving a deficiency of 4·0 p.c.: if this be attributed to water, the base must be regarded as free from oxygen. The hydrochlorate forms with *terchloride of gold* an easily soluble double salt, and with *bichloride of platinum* an unctuous resinous compound (Pfeiffer, *Ann. Pharm.* 128, 275). ¶.

10. Atropine heated with *baryta-water*, is resolved into atropic acid and tropine (Kraut, see page 45):

$$C^{34}NH^{23}O^6 + 2HO = C^{18}H^9O^4 + C^{16}NH^{17}O^4.$$
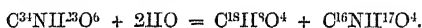
11. An alcoholic solution of *atropine* assumes a blood-red colour when *cyanogen gas* is passed through it, and deposits, on spontaneous evaporation, a red uncrystallisable syrup, insoluble in water (Hinterberger).

Combinations. Atropine dissolves in 300 pts. cold water (v. Planta); 350 pts. (Cap & Garot); 450 pts. at 21° (Brandes); 500 pts. at 19°; daturine in 280 pts. (Geiger & Hesse). It dissolves in 58 pts. boiling water (47 pts. according to Brandes; daturine in 72 pts. according to Geiger & Hesse); and does not separate on cooling; after long boiling it dissolves in 30 pts. water, from which solution a large proportion crystallises out (Geiger and Hesse). Atropine in excess melts in boiling water to an oil (Geiger & Hesse).

Atropine unites with *acids*, forming salts. When an acid is saturated as completely as possible with atropine, the resulting compound is basic, and easily crystallisable; with a smaller quantity of atropine, it is acid, uncrystallisable, and hygroscopic (Geiger & Hesse). Mein & Richter likewise found atropine-salts crystallisable (daturine-salts, according to Geiger & Hesse, crystallise with remarkable beauty), whereas v. Planta & Hinterberger obtained them as syrups, exhibiting little or no tendency to crystallise. — The salts are permanent in the air, have a faint odour, like that of impure atropine, especially in solution, and an extremely bitter taste (Geiger & Hesse). They dissolve very easily in water and alcohol, but are nearly insoluble in ether, which precipitates them from the alcoholic solutions as uncrystallisable syrups (v. Planta). The aqueous solution acquires a dark colour when continuously heated. — The pure fixed alkalis, alkaline carbonates, and caustic ammonia, added to concentrated solutions of atropine-salts, throw down part of the atropine as a pulverulent precipitate, which, (according to Geiger & Hesse), afterwards becomes crystalline, but according to Anderson (*N. J. Pharm.* 13, 443), if produced by ammonia, appears amorphous, even when examined with the microscope. The precipitate dissolves readily in excess of ammonia (Mein); also in excess of caustic potash and carbonate of potash (v. Planta); the alkaline solution is not precipitated by sal-ammoniac (Ludwig); the ammoniacal solution on standing deposits the atropine in crystals. Atropine is not precipitated by carbonate of ammonia, bicarbonate of soda, or phosphate of soda, or by iodic acid, iodide of potassium, or sulphocyanide of potassium (v. Planta). Tincture of iodine produces a kermes-brown precipitate (Geiger & Hesse, v. Planta); bromine dissolved in hydrobromic acid, a light yellow, or in very dilute solutions, a greenish precipitate (Wormley).

Carbonate of Atropine. — An aqueous solution of atropine, if evaporated in contact with the air, absorbs carbonic acid, which it gives off again on addition of acids, or when left to dry up (Geiger & Hesse).

Sulphate of Atropine. — When atropine is not quite neutralised with sulphuric acid, stellate groups of crystals having a satiny lustre are obtained (Geiger & Hesse).

				v. Planta.		
C³⁴NH²³O⁶	 289	....	85·50	.. ..		
SO³	 40	....	11·83	... .	12·19	.... 12·29
HO	 9	....	2·67	....		
C³⁴NH·³O⁶,SO³,HO 338	..... . 100·00					

Biniodide of potassium forms in solution of atropine-salts 100 times diluted, a yellowish precipitate, and in solutions diluted 1000 times or more, a reddish-brown precipitate (Wormley). — Atropine does not combine with perchloric acid (Bodecker, *Ann. Pharm.* 71, 63).

Hydrochlorate of Atropine. — Atropine becomes heated in hydrochloric acid gas, and melts to a transparent yellowish mass, which dissolves in water, with acid reaction, and separates therefrom in radiate groups of shining needles, permanent in the air (Liebig). 100 pts. atropine take up 13·85 pts. hydrochloric acid (v. Planta), (1 at. = 12·6 pts.). — The solution of atropine in hydrochloric acid dries up to a clear varnish, which, after a few days' exposure to a temperature of 30°—40°, forms crystalline stars. By subsequent exposure to the ordinary temperature of the air for two weeks, these crystals are converted into light tufts of needles, permanent in the air, and perfectly soluble in water, the solution exhibiting a weak alkaline reaction (Geiger & Hesse).

				v. Planta.		
C³⁴NH²³O⁶	.... 289·0	....	88·79	.... .		
HCl	.... 36·5	... ...	11·21	....	10·17	.... . 10·76
C³⁴NH²³O⁶,HCl .... 325·5	.... 100·00	....				

Nitrate of Atropine. — The solution dries up on evaporation to a varnish, which, in contact with the air, becomes moist and soft, but not coloured (Geiger & Hesse).

Phosphantimonic acid (xiv. 227) produces, in solutions containing $\frac{1}{1000}$ atropine, a white precipitate, which cakes together strongly, dissolves at first when heated, but appears again in considerable quantity on prolonged boiling, and is then insoluble, even in a large quantity of water (F. Schulze, *Ann. Pharm.* 109, 179). — With *phosphomolybdic acid* (xiii. 164) atropine forms a light-yellow flocculent precipitate (Sonnenschein).

Potassio-mercuric iodide forms with atropine-salts a dense curdy precipitate, which cakes together on adding hydrochloric acid (v. Planta, Delffs). — *Mercuric iodide* does not precipitate hydrochlorate of atropine (v. Planta); it forms a white precipitate, which coheres into a plaster-like mass, even in strongly cooled liquids (Hinterberger).

Chloro-aurate of Atropine. — From hydrochlorate of atropine terchloride of gold throws down a sulphur-yellow crystalline precipitate

(Mein ; v. Planta). Solutions containing $\frac{1}{1000}$ atropine in the form of acetate, yield greenish-yellow precipitates (Wormley). — To prepare the gold-salt, a strong solution of hydrochlorate of atropine is dropped, with agitation, into a dilute solution of chloride of gold, whereupon the precipitate, which is pulverulent at first, soon changes to a dense crystalline pulp of a fine yellow colour, and easy to wash. After drying in vacuo, it does not lose weight at 120° ; begins to melt at 135°. The salt prepared with atropine obtained from *Datura*, melted between 90° and 100°, but did not decompose even at 160°. Slightly soluble in water and in hydrochloric acid (v. Planta).

				v. Planta.	
				a.	mean.	b.
34	C	204·00	.... 32·45	.... 31·79	... 32·75
	N	14·00	.... 2·22		
24	H	24·00	.. 3·81	.... 3·97	.... 4·43
6	O	48·00	.... 7·63		
4	Cl	141·84	.... 22·58		
	Au	196·66	.... 31·31	... 31·39	.... 31·36

$C^{24}NH^{23}O^6,HCl,AuCl^3$ ...... 628·50 . 100·00

a obtained from *Atropa ;* *b* from *Datura.*

Bichloride of platinum throws down from highly concentrated solutions of hydrochlorate of atropine, thick yellow flocks which cohere into a resinous mass, very soluble in hydrochloric acid (v. Planta). — *Chloriridiate of sodium* produces no precipitate (v. Planta).

Acetate of atropine gives off acetic acid when left to evaporate, and leaves crystals no longer perfectly soluble in water (Geiger & Hesse). — *Tartrate of atropine* is not crystallisable (Geiger & Hesse). — *Rhodizonate of atropine* is hyacinth-red, easily soluble in water and alcohol. — *Croconate of atropine* is a yellow bitter mass (Heller, *J. pr. Chem.* 12, 229).

Valerate of Atropine. — Atropine is triturated at 0° with an equivalent quantity of valerianic acid mixed with twice its weight of ether, and cooled to 0° ; a further quantity of ether equal to 5 times the weight of the atropine is added; the whole is cooled, after filtration if necessary, in a closed vessel, to — 10° ; and the crystals which form after two hours are freed from the mother-liquor by decantation, and then washed with absolute ether (Gallmann). Miette's process (*Compt. rend.* 45, 1052; *J. pr. Chem.* 73, 503), which consists in neutralising alcoholic atropine with valerianic acid, and leaving the solution to evaporate, yields nothing but an uncrystallisable syrup, containing atropine in small quantity only, or in an altered state. — Light white crusts, or more distinctly formed, apparently rhombic crystals, colourless, transparent, and strongly refracting. Slightly alkaline in aqueous, neutral in ethereal solution. Remains unaltered when kept in close vessels at a temperature somewhat below 20°, softens somewhat above 20°, and melts at 42° to a colourless syrup, which does not solidify even at very low temperatures. Gives off water of crystallisation at 100°, valerianic acid also at 120°, and when more strongly heated, emits, first acid, afterwards strongly alkaline vapours. When exposed to the air, it smells of valerianic acid. In very moist air it deliquesces to a syrup, which quickly becomes light yellow on exposure to light. Dissolves very easily in water and in

alcohol, but does not crystallise from the solution. Dissolves with difficulty in ether (Callmann, *J. pr. Chem.* 76, 69 ; *N. J. Pharm.* 34, 345).

						Callmann. mean.
44	C	264	....	66·0	....	66·31
	N	14	....	3·5	... .	
34	H	34	... .	8·5	....	6·85
11	O	88	... .	22 0	. ..	
	$C^{34}NH^{23}O^6,C^{10}H^{10}O^4 + HO$	400	....	100 0	....	

Atropine-salts form a sulphur-yellow pulverulent precipitate with *picric acid* (v. Planta). With very dilute solutions the precipitate is greenish (Wormley).

Infusion and *tincture of galls* throw down from atropine-salts and alcoholic atropine, white curdy flocks partially soluble in ammonia (Geiger & Hesse ; Mein ; Henry).

Atropine dissolves in cold aqueous solution of the *fixed alkalis*, but not more abundantly than in water, and is extracted from these solutions by ether (Geiger & Hesse). In aqueous *ammonia* it dissolves when heated (Brandes).

Atropine dissolves in 8 pts. of cold *alcohol* (Geiger & Hesse), in 4 or 5 pts. (Brandes), in 2 pts. (Cap & Garot), in nearly all proportions (v. Planta). In warm alcohol it dissolves more abundantly, without separating out on cooling (Geiger & Hesse). It is precipitated from the alcoholic solution by water (Mein ; Henry). The alcoholic solution forms a jelly on spontaneous evaporation (Richter). — Atropine dissolves in 63 pts. cold ether (36 pts according to Brandes) and 42 pts. warm ether, the solution not becoming turbid on cooling (Geiger & Hesse). — It dissolves in 50 pts. *glycerin* (Cap & Garot) ; in 1·93 pts. *chloroform* (M. Pettenkofer), in 3 pts. (Schlimpert), in 35 pts. *fixed oil* (Cap & Garot), 38·2 pts. *olive-oil* (Pettenkofer), in *oil of turpentine* when heated (Brandes). — It is withdrawn from its solutions by *animal charcoal* (Geiger & Hesse).

Appendix to Atropine.

Hyoscyamine,

G EIGER & H ESSE. *Ann. Pharm.* 7, 270.

The earlier attempts of Brandes (*Schw.* 28, 91 ; *Ann. Pharm.* 1, 333) and of Bley (*N. Tr.* 20, 2, 157), to isolate the active principle of *Hyoscyamus niger* were unsuccessful. See Dobereiner (*Schw.* 38, 105), Lindbergson (*Scher. Ann.* 8, 60).

Preparation. Henbane seed is exhausted with hot water or alcohol ; the extracts are evaporated at a gentle heat, purified by repeated treatment with lime and sulphuric acid, and subsequent filtration (See atropine); the moderately decolorised and concentrated extracts are mixed with pulverised crystallised carbonate of soda ; the precipitate is freed as quickly as possible from fixed alkali by pressure and treatment with absolute alcohol ; the mother-liquor is at the same time treated with ether ; the ethereal and alcoholic extracts are mixed, again treated with lime and filtered ; the filtrate is treated with animal charcoal ; the

greater part of the ether and alcohol are distilled off; and the liquid is finally evaporated at a very gentle heat, with addition of water. If the hyoscyamine thus obtained is coloured, it must again be combined with acids and treated as above (Geiger & Hesse).

Hyoscyamine crystallises slowly in tufts of colourless transparent silky needles. Inodorous. It is often obtained in the amorphous state, difficult to dry, coloured, having a narcotic odour, and soluble in any quantity of water. — It has a very nauseous biting taste, like that of tobacco, and exerts a very strong narcotic action, like that of atropine, and likewise produces persistent dilatation of the pupil. — On addition of water, it acquires a strong and permanent alkaline reaction. — When cautiously heated, it volatilises for the most part undecomposed; at all events it afterwards exhibits an equally strong poisonous action, and is still strongly alkaline; nevertheless a portion is destroyed, with evolution of ammoniacal vapours. A small portion appears also to volatilise when it is boiled with water, as the distillate is slightly alkaline and dilates the pupil.

By heating with aqueous *alkalis*, it is completely decomposed, with evolution of ammonia.

It dissolves sparingly in *water*, but more freely than atropine. The aqueous solution mixed with *tincture of iodine*, thickens and becomes crimson; it forms a yellowish-white precipitate with solution of *gold*, a copious white precipitate with *tincture of galls*, and is not precipitated by *chloride of platinum*.

The *salts of hyoscyamine* are neutral, and some of them crystallise readily.

Hyoscyamine is very soluble in *alcohol* and in *ether*.

¶. *Appendix to* vol. xiii. p. 239.

Tropine.

$$C^{16}NH^{17}O^4 = C^{16}AdH^{15}O^4, H^2?$$
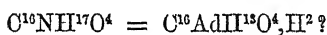
KRAUT. *Ann. Pharm.* 128, 282.

Produced, together with atropic acid, by the decomposition of atropine under the influence of hot baryta-water (p. 453):

$$C^{34}NH^{23}O^6 + 2HO = C^{18}H^8O^4 + C^{16}NH^{17}O^4.$$
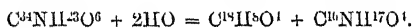
The same products appear to be formed when atropine is heated with fuming hydrochloric acid.

Preparation of Atropic Acid and Tropine. — When atropine is heated to 100° in a sealed tube with a saturated solution of baryta, the oily layer which at first floats on the surface disappears in the course of 2 or 3 hours. The clear colourless solution distilled, after addition of water, gives off only traces of a volatile base, and on passing carbonic acid through the remaining liquid, nearly all the baryta is precipitated as carbonate free from organic substance. On evaporating the neutral filtrate, atropate of tropine remains as an amorphous vitreous mass, which, on standing over oil of vitriol, deposits traces of

atropate of baryta. The aqueous solution of atropate of tropine becomes milky on addition of dilute hydrochloric acid, and after a few seconds deposits crystals of atropic acid, while hydrochlorate of tropine remains dissolved, and may be separated from the atropic acid by agitation with ether, which takes up the acid.

When the solution of hydrochlorate of tropine, obtained as above, is slowly evaporated, the salt crystallises in needles, which redissolve easily in water. The solution treated with oxide of silver becomes strongly alkaline, and when filtered and evaporated, leaves a crystalline residue, which however is found to have absorbed carbonic acid, and appears also to have suffered further alteration, so that the base has not yet been obtained in the pure state. — It appears also to be decomposed when heated with *baryta-water* to 180°—190° for 17 hours; but the decomposition is not complete, and the product is not volatile. — When the aqueous solution of tropine is boiled for some time, small quantities of the base volatilise : hence probably it arises that tropine boiled with baryta-water yields a slightly alkaline distillate (p. 457), while traces of atropate of baryta remain in solution.

Tropine is soluble in *water*.

The *hydrochlorate* crystallises in needles.

The *chloro-aurate*, obtained by mixing the aqueous solution of the hydrochlorate with chloride of gold, crystallises easily.

Chloroplatinate. Precipitated by bichloride of platinum from the solution of the hydrochlorate; dissolves on heating the liquid, and separates on cooling in beautiful orange-red crystals, which may be ground to a reddish-yellow powder.

						Kraut. mean.
16	C	96·0	......	26·28	......	25·27
	N	14·0	......	3·83	......	
18	H	18·0	......	4·93	......	4·84
4	O	32·0	......	8·76	......	
3	Cl	106·5	......	29·16	......	
	Pt	98·7	......	27·01	......	27·33
$C^{16}NH^{17}O^4,HCl,PtCl^2$		365·2	......	100·00	......	

Tropine likewise combines with *atropic acid*.

Appendix to vol. xiii, p. 268.

Atropic Acid.

$$C^{18}H^8O^4 = C^{18}H^8,O^4.$$
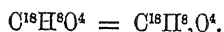
KRAUT. *loc cit.*

Formation and Preparation (p. 457).

Crystallises readily from alcoholic solution in tables belonging to the oblique prismatic system, permanent in the air; from water in needles having the odour of benzoic acid, and melting to an oil at $107\frac{1}{2}°$. The hot saturated aqueous solution has a strong acid reaction,

and on cooling, first becomes milky, then yields oil-drops, and solidifies when quite cold to a crystalline pulp.

		Over oil of vitriol.			Kraut.
18 C	....	108	....	72·97	.... 72·34
8 H	....	8	....	5·41	.... 5·51
4 O	....	32	....	21·62	.... 22·15
$C^{18}H^8O^4$	....	148	....	100·00	. ... 100·00

Isomeric with cinnamic acid (xiii, 268). — The acid which Pfeiffer (p. 452) obtained by heating atropine with soda-ley is probably atropic acid.

Atropic acid is soluble in *water*. It appears to be monobasic.

Atropate of Lime forms remarkably fine crystals (obtained, however, in small quantity only, and perhaps not quite pure), which, at 115° over oil of vitriol, give off 13·94 p. c. water, the residual salt then yielding 14·36 p. c. lime ($C^{16}H^7CaO^4 + 3aq = 14·43$ p. c. CaO).

Atropic acid dissolves in *alcohol*.

Atropate of Tropine. Preparation, p. 437). Uncrystallisable; ropy and scarcely fluid at common temperatures, deliquesces in a warm atmosphere. Contains 3 at. water, of which 2 at. (calc. = 5·38 p. c.) go off at 90°. A solution containing 2·23 p. c. of the salt does not dilate the pupil.

					Kraut.
34 C	....	204	....	61·07	.... 60·92
N	....	14	....	4·19	....
28 H	....	28	....	8·39	.... 8·89
11 O	....	88	....	26·35	....
$C^{16}NH^{17}O^4,C^{18}H^8O^4 + 3aq.$	....	334	....	100·00	.... ¶

Primary Nucleus $C^{34}H^{30}$; *Oxygen-nucleus* $C^{34}H^{24}O^6$.

Cotton-seed Blue.

$$C^{34}H^{24}C^8 = C^{34}H^{24}O^6,O^2?$$
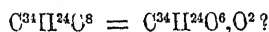
Fr. Kuhlmann. *Compt. rend.* 53, 444.

Formation. In the purification of cotton-seed oil on the large scale, which is effected by the prolonged action of soda-ley or milk of lime, a greasy deposit is formed, from which, when boiled for several hours with sulphuric acid of 10° B. the enclosed fats separate as a supernatant oily layer. When this oil is heated alone, to drive off adhering water, the adhering sulphuric acid being at the same time concentrated, a bluish-green deposit collects at the bottom of the vessel, and solidifies on cooling, while the supernatant oil remains green. This deposit contains the cotton-seed blue, which is not perceptible in the seeds themselves, its colour becoming apparent only when they are heated with phosphoric acid, oil of vitriol, or strong hydrochloric acid.

Preparation. The above-mentioned deposit is heated to 100° with 3 or 4 p. c. oil of vitriol for five or six hours, or till it has become black-blue, and the product is freed from the greater part of the acid by washing with warm water, and from the rest by solution in alcohol, and precipitation by water. From the mixture of cotton-seed blue and fatty acids thus obtained, the acids are dissolved out by continued washing with rock-oil, which dissolves a small portion of the blue, only so long as fatty acids are still present.

Properties. Amorphous blue grains or flocks, which do not melt.

		at 100°.						Kuhlmann.
34	C	204	.....	69·87	....	70·16	....	70·02
24	H	24	....	8·22	......	8·17	......	8·54
8	O	64	.....	21·91	....	21·37	.....	21·44
C³⁴H²⁴O⁸	....	292	.....	100·00	......	100·00	....	100·00

Decompositions. 1. Cotton-seed blue *takes fire* when heated on platinum-foil, and leaves a difficultly combustible cinder. — 2. It is not altered by reducing agents, such as hydrogen, sulphurous acid, ferrous oxide, stannous oxide, or arsenious acid, but is immediately decomposed by oxidising agents, such as chromic acid, ferric hydrochlorate, nitric acid, chlorine, bromine, and iodine (see below). — 3. When the pulverised blue is thrown by small portions into strong *nitric acid*, a solid yellow mass is formed, which must be triturated with fresh nitric acid, in order to ensure complete conversion. The compound thus formed contains (at 100°) 60·28 p. c. C., and 6·76 H., together with nitrogen and oxygen, corresponding with the formula C³²XH²⁴O⁸; it is insoluble in water, but dissolves easily in aqueous alkalis, whence it is precipitated by acids, also in alcohol and ether, and is deposited in the granular form on cooling from hot saturated solutions. From the ammoniacal solution of this nitro-compound, nitrate of silver and neutral acetate of lead throw down granular precipitates. — 4. When *chlorine-gas* is passed into the alcoholic solution of the blue till the colour disappears, amorphous yellow flocks are precipitated, which, after being purified by solution in hot alcohol, contain 11·47 p. c. chlorine, and are therefore C³⁴ClH²³O⁸ (calc. 10·87 p. c. Cl.). — 5. Cotton-seed blue kept in contact for a week, or boiled for several hours, with *alcohol* or *ether*, acquires a green or brown colour; on boiling it with *oil of turpentine*, this change takes place immediately; *sulphide of carbon* produces it more slowly than alcohol or ether.

Cotton-seed blue is insoluble in *water*, and in boiling aqueous *phosphoric, hydrochloric*, or *acetic acid*. — It dissolves with purple colour in *oil of vitriol*, and is precipitated by water in its original state. — It is insoluble in cold aqueous *alkalis*, but dissolves in them at the boiling heat, with faint green colour, and is precipitated in blue flocks by acids. — Sparingly soluble in *sulphide of carbon* and in *chloroform ;* in 77 pts. *alcohol* of 90 p. c. at 20°, and in 8⅓ pts. *ether.* In presence of fatty acids it dissolves with greater facility. The alcoholic solution dyes fabrics either unmordanted or mordanted with alum, a fine blue colour, quickly fading, however, on exposure to light and air.

Oxygen-nucleus $C^{34}H^{18}O^{12}$.

Aloïn.

$$C^{34}H^{18}O^{14} = C^{34}H^{18}O^{12},O^2.$$
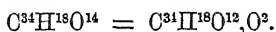
T. & H. Smith. *Chem. Gaz.* 1851, 107; *N. J. Pharm.* 19, 275; abstr. *Lieb. Kopp's Jahresber.* 1850, 645.
Stenhouse. *Phil. Mag. J.* 37, 481; *Ann. Pharm.* 77, 208; *J. pr. Chem.* 52, 149; abstr. *Lieb. Kopp's Jahresber.* 1850, 545.
Robiquet. *N. J. Pharm.* 29, 241; *Pharm. Viertelj.* 5, 555; *N. Repert.* 5, 369; abstr. *Lieb. Kopp's Jahresber.* 1856, 679.
Groves. *Pharm. J. Trans.* 16, 128; *N. J. Pharm.* 31, 367; abstr. *Lieb. Kopp's Jahresber.* 1856, 680.

Discovered by Smith; more exactly investigated by Stenhouse. Occurs in Barbadoes aloes (Smith). Smith did, according to Robiquet, not succeed in preparing aloïn from soccotrine or Cape aloes, because these varieties (which are transparent and vitreous) contain amorphous aloïn (=*aloëtin*) whereas crystalline aloïn occurs only in the opaque varieties. But Groves obtained crystallised aloïn likewise from soccotrine aloes, and Stenhouse supposes it to exist in all those varieties of aloes which yield chrysammic acid when treated with nitric acid. — The microscopic crystals observed by Pereira (*N. Repert.* 1, 467) in liquid aloe-juice, consist, according to Robiquet, of aloïn. To separate them by filtration, it is necessary first to stir up the juice with water containing 10 or 12 drops of aqueous ammonia in a litre, which will dissolve the resin (Robiquet). Crystals are also found in Indian aloes, in liver aloes, and in the fresh juice of old leaves of *Aloe vulgaris* (Schroff, *N. Repert.* 2, 49).

Aloes was examined some years ago by Tromnsdorff (*N. Tr.* 14, 1, 297), Bouillon-Lagrange & Vogel (*J. Phys.* 68, 160) and Pfaff, who described the aqueous extract of aloes as *Bitter* and *Resin of aloes.* Braconnot (*Ann. Chim.* 68, 24. — *J. Phys.* 84, 335), distinguished a substance precipitated by oxide of lead from the aqueous extract of aloes, as *Principe puce aloetique;* it is a tasteless and scentless powder, and is precipitated from the alcoholic solution by water. Meissner (*N. Tr.* 6, 1, 225), by precipitating the aqueous extract of aloes with a lead-salt, treating the filtrate with hydrosulphuric acid, evaporating, and treating the residue with sulphuric acid, obtained a crystallisable salt soluble in water (of organic nature ?). — Robiquet's *aloëtin* or *pure aloes* (*N. J. Pharm.* 10, 173), is obtained as follows:—Extract of aloes prepared with cold water is precipitated by neutral acetate of lead; the precipitate is removed; the filtrate mixed with ammonia; and the precipitate, after washing with boiling water, is decomposed by hydrosulphuric acid. The colourless liquid evaporated in a vacuum leaves aloëtin as a pale yellow, scaly, varnish-like residue, whose aqueous solution reacts with alkalis and with neutral acetate of lead in the same manner as aloïn. This aloëtin, which Robiquet afterwards regarded as amorphous aloïn, contains 27·39 p. c. C., 11·11 H., and 61·50 O. — On *bitter of aloes,* see also Winckler (*N. Tr.* 22, 1, 67); on *resin of aloes,* Bley (*N. Tr.* 24, 2, 112), and Buchner (*Repert.* 94, 374).

According to Kosmann (*N. J. Pharm.* 40, 177; *Pharm. Viertelj.* 11, 232) Cape aloes is separated by cold water into a soluble and an insoluble portion, each of which may be resolved, by boiling with dilute sulphuric acid, into sugar and new substances. This fact, and the separate identity of the products of decomposition described by Kosmann, viz., *Aloëresinic, Aloëretinic, Aloëressic,* and *Aloëretic acids,* which are to be distinguished from the similarly-named products of other chemists, do not appear to be satisfactorily demonstrated (Kr.).

Rochleder has described *crystals from soccotrine aloes* which must be distinguished from aloïn. When the solution of *Aloe soccotrina* in dilute soda-ley is heated to boiling, till the strong frothing which takes place at first has subsided (whereupon small quantities of a volatile base and a volatile oil pass over) and the clear alkaline solution is mixed with sulphuric acid. and shaken up with ether, the ether acquires a yellow colour, and leaves a crystalline residue when evaporated. This residue is dissolved in boiling water, which leaves resin behind; the solution is decolorised with animal charcoal; and the filtrate is left to cool, whereupon it deposits colourless crystals an inch long. These crystals volatilise without residue, and form a colourless solution with alkalis. Rochleder & Czumpelick (*Wien. Akad. Ber.* 44, 493; *Chem. Centr.* 1862, 5).

Preparation of Aloïn. 1. Barbadoes aloes dried and comminuted with sand is exhausted with cold water; the solution is evaporated in a vacuum to a syrup; and the residue is left at rest for three or four days in a cold place, whereupon it yields brownish yellow crystalline granules. These are quickly pressed between paper, and repeatedly crystallised from water at a temperature not exceeding 65°, till they retain only a pale sulphur-yellow colour, and no longer suffer any change of colour when dried in the air (Smith, Stenhouse). The aqueous solution, when evaporated over the water-bath, does not yield any aloïn (see below), because the impurities, which undergo oxidation at the same time, interfere with the crystallisation; the crystals likewise disappear when left for some time in the mother-liquor, which at the same time acquires a darker colour (Stenhouse).—2. One part of Barbadoes aloes is drenched in a covered vessel with 2 pts. of water deaërated by boiling; and the liquid is rapidly stirred, decanted after a quarter of an hour, covered with a layer of ether to protect it from the air, and left to itself for a month. The nodules which then separate are a mixture of crystals of aloïn, amorphous aloëtin, and earthy impurities; they are purified by successive washing with cold water and alcohol of 56 p. c., the washing with the latter being continued as long as the liquid which runs off exhibits a reddish yellow colour, — and finally by recrystallisation from alcohol of 86 p. c. (Robiquet). — 3. Coarse powder of soccotrine aloes is added to boiling water; the liquid is left to stand for 20 minutes, stirred from time to time, and filtered after cooling; and the filtrate, after being acidulated with hydrochloric acid, is again filtered to separate resin, and evaporated over the water-bath to a syrup, which, after standing for a week or longer, deposits crystals of aloïn (Groves).

Properties. The hydrated crystals (p. 463) are rendered anhydrous by drying for five or six hours over the water-bath. — Tastes

sweetish at first, then intensely bitter. Inodorous. Neutral (Stenhouse ; Smith). According to Stenhouse, it exerts a strong purgative action ; according to Robiquet, only after it has been converted by heat into amorphous aloëtin.

						Stenhouse. mean.
34 C	... ...	204	... ...	61 07	....	60 63
18 H	...	18	... .	5 39	... ...	5·58
14 O	.	112	. .	33 54	. ..	33·79
$C^{34}H^{18}O^{14}$	... ...	334	....	100 00	.. ..	100·00

Decompositions. 1. Aloïn, after drying for 6 hours, loses an additional quantity of water when left over the water-bath for several days, and is converted into a resin ; the same change takes place much more quickly at 150°, the aloïn then melting to a dark brown mass which becomes hard and brittle on cooling. This mass consists of amorphous resin, still mixed with a large quantity of crystallisable aloïn, which may be extracted by alcohol. — 2. By *dry distillation* it yields a volatile aromatic oil and a larger quantity of resin. — 3. Aloïn heated on platinum-foil melts and *burns* with a bright yellow flame, depositing a large quantity of soot, and leaves a difficultly combustible cinder (Stenhouse). — 4. The *aqueous solution* oxidises quickly at 100° (Stenhouse). Boiling alcohol and ether likewise alter aloïn and render it uncrystallisable (Robiquet). — 5. *Chlorine gas* separates from the cold aqueous solution, a deep yellow, resinous, uncrystallisable precipitate, richer in chlorine (Stenhouse). Respecting the action of chlorine upon aloes see p. 465. — 6. *Bromine* added to a cold aqueous solution of aloïn throws down bromaloïn aloïn and forms hydrobromic acid (Stenhouse). — 7. Aloïn gradually added to cold *fuming nitric* acid, dissolves without evolution of nitrous gas, forming a brown-red liquid, whence oil of vitriol added in large quantity, throws down a yellow detonating compound, which does not crystallise, and is decomposed by solution in alcohol (Stenhouse). — Cold nitric acid (also sulphuric or hydrochloric acid) colours aloïn lemon-yellow (Robiquet) ; after boiling for half an hour, or digestion for a longer time, a large quantity of nitrous gas is given off, and chrysammic acid (xii, 1) is formed, unmixed with picric acid (Stenhouse, Robiquet). — On the action of *nitric acid upon aloes*, see xi, 211 (picric acid) ; xii, 1 (chrysammic acid) ; xii, 9 (aloeretic acid), and xii, 10 (aloetic acid). — 8. When aloïn is boiled with *chlorate of potash* and *hydrochloric acid*, the solution evaporated, and the residue treated with alcohol, the resulting alcoholic solution leaves on evaporation a non-crystallising syrup, which does not contain chloranil (Stenhouse). — 9. Aloïn boiled with strong *acids* or *alkalis*, is quickly converted into a dark brown resin ; the deep orange-yellow solution of aloïn in cold caustic ammonia, potash, or soda, or their carbonates, likewise quickly acquires a darker colour by incipient oxidation (Stenhouse). — On the distillation of aloes with lime, see xii, 214.

Combinations. With *Water.* — *Crystallised Aloïn.* — Separates from water in sulphur-yellow grains ; from hot alcohol in stellate groups of needles (Stenhouse).

		In vacuo.			Stenhouse. mean.
34	C	204	59·47		59 32
19	H	19	5 54		5 88
15	O	120	34·99		34 80
$C^{34}H^{18}O^{14}$ + aq		343	100·00		100 00

Sparingly soluble in cold *water* (Stenhouse), in 600 pts. (Smith), 10 pts. at 10° (Robiquet). — Dissolves easily in cold aqueous *ammonia*, *potash*, *soda*, or their carbonates, forming deep orange-coloured solutions (Smith, Stenhouse). The concentrated aqueous solution (not the dilute solution) forms, with *basic acetate of lead*, a deep yellow precipitate, which dissolves in water and turns brown in contact with the air. Aloïn does not precipitate *neutral acetate of lead, mercuric chloride*, or *nitrate of silver* (Stenhouse).

Aloïn dissolves readily in *alcohol* and in *acetate of ethyl* (Smith, Stenhouse) in 2 pts. alcohol of 86°, and in 8 pts. *ether* (Robiquet).

Oxybromine-nucleus $C^{34}Br^3H^{15}O^{12}$.

Bromaloïn.

$$C^{34}Br^3H^{15}O^{14} = C^{34}Br^3H^{15}O^{12},O^2.$$
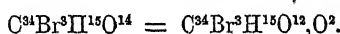
STENHOUSE. *Ann. Pharm.* 77, 212.

A cold aqueous solution of aloïn is mixed with excess of bromine, and the yellow precipitate is washed with water and dissolved in hot alcohol, which deposits crystals on cooling.

Yellow, shining needles, grouped in stars, larger and darker than those of aloïn. Neutral. — Less soluble than aloïn in cold water and alcohol, very soluble in hot alcohol.

		In vacuo.			Stenhouse. mean.
34	C	204	35·73		35·48
3	Br	210	42 02		41·97
15	H	15	2·62		2 78
14	O	112	19·63		19 77
$C^{34}Br^3H^{15}O^{14}$		571	100·00		100·00

Appendix to Aloïn.

1. *Chloraloil.* — Obtained, together with a brown resin and a blue substance, by passing chlorine into aqueous aloïn. — When chlorine-gas is passed into a cold-prepared solution of soccotrine aloes, till the liquid and the separated flocks, which are yellow at first, have acquired a green colour, and the acid solution is decanted, a resinous laminar substance is found deposited on the sides of the vessel; this is collected, washed with boiling water, then with cold alcohol, and dissolved in boiling alcohol. On concentrating and cooling the solution,

the chloraloïl crystallises out, and may be purified by washing with cold, and recrystallisation from boiling alcohol (sometimes only a trace is obtained). — Snow-white, light, silky needles, which melt at 140° to a transparent liquid, solidifying in the crystalline form on cooling. Boils at 155°, distilling over without residue, and condensing in the neck of the retort. Contains 50·65 p. c. C., 23·33 Cl., and 26·02 O., no hydrogen, corresponding therefore with the formula $C^{13}ClO^5$ (Robiquet). Dissolves, with decomposition, in *nitric, sulphuric,* and *acetic acids,* forming yellow solutions. By boiling or fusion with *alkalis,* it is completely converted into alkaline carbonate and chloride. Dissolves easily in *baryta-water,* forming a purple-red solution, which, when left to evaporate freely, gradually loses its colour, and deposits crystals of chloride of barium. *Ammonia* dissolves chloraloïl abundantly, acquiring a yellow and then a red colour, and depositing, on addition of acids, yellow flocks, differing altogether in comparison from chloraloïl. The ammoniacal solution, evaporated at a gentle heat, yields nothing but crystals of sal-ammoniac. — Chloraloïl is nearly insoluble in cold *water* and *alcohol,* but hot alcohol dissolves it in such quantity that the solution solidifies to a jelly on cooling; it is also very soluble in *ether.* (Robiquet, *N. J. Pharm.* 10, 249; *J. pr. Chem.* 39, 189; abstr. *N. Ann. Chim. Phys.* 20, 490).

2. *Chloralise.* Chlorine-gas is passed through an alcoholic solution of aloes, till the liquid, which is at first very dark-coloured, has become pale yellow, and the solution is heated in a shallow dish for two hours to 60°—80°, to expel hydrochloric acid, aldehyde, and other products. The remaining liquid, mixed with twice its volume of cold water, deposits chloralise as a copious yellow precipitate, which is collected, separated by solution in boiling water, and repeated filtration through a wet filter, finally obtained on cooling as a yellow powder, and purified by washing with cold ether, and recrystallisation from boiling alcohol. Slender, sulphur-yellow, flexible needles, having a strong silky lustre. Inodorous. Melts at 70°, without decomposition or loss of water. Contains, on the average, 55·64 p. c. C., 3·84 H., 32·26 Cl., and 8·26 O., agreeing with the formula $C^{10}ClH^4O.$ — At 180° it swells up strongly, and acquires a brown-red colour, and at 200° decomposes completely, giving off hydrochloric acid and a brown oil. Dissolves easily in *nitric, sulphuric,* and *hydrochloric acids,* and is precipitated unaltered from the recently prepared solution by water. — *Dissolves* in caustic *ammonia, potash,* and *soda,* forming brown-yellow solutions, from which acids throw down orange-yellow flocks, altogether different from chloralise. — Dissolves sparingly in cold *water;* in all proportions in boiling water and in *alcohol;* slightly in *ether,* whether cold or warm (Robiquet).

Primary Nucleus $C^{34}H^{32}$; *Oxygen-nucleus* $C^{34}H^{28}O^4$.

Gratiolaretin.

$? \ C^{34}H^{28}O^6 = C^{34}H^{28}O^4,O^2.$

WALZ. *N. Jahrb. Pharm.* 10, 67.

Formation, p. 467.

Preparation. Gratiolin is boiled with dilute sulphuric acid as long as the liquid tastes bitter, the gratiolin, which is at first suspended in the liquid, gradually disappearing, with formation of oily gratiolaretin, crystalline gratioletin, and sugar which remains dissolved. The solution is filtered, the residue washed, and the gratiolaretin extracted from it by ether, which it leaves behind on evaporation. — Gratioletin remains on the filter.

Properties. Soft, amorphous, yellow mass, becoming brittle and easily friable by prolonged exposure to a warm atmosphere. Tasteless, but has a faint resinous odour. Melts below 100°.

		at 120°.			Walz.
34 C ..	 204	.....	72·87	. 71·45 .	73·12
28 H .	 28	.....	10 00	... 10 22 ..	10 27
6 O	.. 48	...	17 13	18 33 ..	16·61
$C^{34}H^{28}O^6$ 280	..... 100·00		... 100 00	. .. 100 00

Not altered by *oil of vitriol*, even at 100°. — Dissolves in *nitric acid* of sp. gr. 1·54, without evolution of gas, forming a solution precipitable by water.

Insoluble in *water*, easily soluble in *alcohol* and in *ether*.

Glucosides of Gratiolaretin.

1. Gratiolin.

$C^{40}H^{34}O^{14}$.
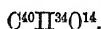
Eug. Marchand. *J. Chim. méd.* 21, 517; *Repert.* 91, 372.
G. F. Walz (1852). *Jahrb. pr. Pharm.* 14, 4; 21, 1; 24, 4; *N. Br. Arch.* 65, 192. — *N. Jahrb. Pharm.* 10, 65.

The bitter principle of *Gratiola officinalis.*

Preparation. 1. The ethereal extract of gratiola is exhausted with alcohol; the solution is evaporated; the residue [Vauquelin's *Matière resinoïde amère* (*Ann. Chim.* 72, 191)] is redissolved in alcohol; ferric sulphate is added as long as it acquires a blue colour, then thin milk of lime in quantity sufficient to saturate the free acid and precipitate the excess of ferric oxide; and the filtrate, decolorised if necessary by animal charcoal, is evaporated in a vacuum. The residue is freed from the greater part of the admixed salts by treating it with a small quantity of water—which, however, likewise dissolves a portion of the gratiolin—the undissolved matter is shaken up with ether containing water; the ethereal solution is removed; and the subjacent syrup, diluted with alcohol, is left to evaporate by exposure to the air, whereupon gratiolin remains in white nodules. When thus prepared, it still retains a small quantity of ash (Eug. Marchand). — 2. The aqueous decoction of the dried plant is precipitated with basic acetate of lead, and strained through linen; the filtrate is mixed with car-

bonate of soda, not in excess; the precipitated carbonate of lead is removed; and the filtrate is precipitated with aqueous tannic acid. The precipitate is collected, washed, strongly pressed, triturated, after partial desiccation, with hydrated oxide of lead (basic acetate of lead, or litharge, or the latter with 5 p. c. basic acetate, may likewise be used), then covered with alcohol of sp. gr. 0·85, and set aside till a sample of the alcoholic solution is no longer turned blue by sesqui-chloride of iron. The solution is filtered, the residue repeatedly digested with alcohol, as long as it imparts a bitter taste; the united tinctures are decolorised by leaving them in contact with animal charcoal; the greater part of the alcohol is distilled off, after filtration from the charcoal; and the remaining liquid is evaporated to dryness. The residue is exhausted successively with absolute ether and cold water, then dried and recrystallised from boiling alcohol or boiling water. The ether takes up chiefly gratiolacrin, the cold water gratiosolin. — If the gratiolin thus obtained is coloured, it may contain gratiosolin, or a brown resin. It must then be dissolved in a small quantity of alcohol, and precipitated by water, which leaves the gratiosolin in solution; and the precipitated gratiolin freed from resin by digestion with ether, or (in case the resin present is insoluble in ether), by dissolving it in alcohol, precipitating with alcoholic sugar-of-lead, removing the excess of lead from the filtrate, evaporating, and recrystallising from boiling water (Walz).

Properties. White powder, crystallising from alcohol in nodules (Marchand), from water in slender needles having a satiny lustre (Walz). Taste scarcely perceptible at first, afterwards strongly bitter. Has a faint odour. Melts at 200° without further alteration; softens when heated with water, and rises to the surface as an oil (Marchand). —Produces no particular effect upon rabbits.

					Marchand.		
					earlier.		later.
40 C	......	240	......	62·17	......	61·25	...... 62·00
34 H	......	34	......	8·81	......	9·41	...... 9 38
14 O	......	112	......	29·02	......	29·34	...... 28 62
$C^{40}H^{34}O^{14}$	......	386	......	100·00	......	100·00	...... 100 00

Walz formerly gave the formula $C^{42}H^{36}O^{14}$.

Decompositions. 1. Turns brown and decomposes at 212°, and when *heated* on platinum-foil, gives off acid vapours, takes fire and burns away. — 2. By prolonged boiling with *dilute sulphuric acid*, it is resolved with gratioletin, gratiolaretin, and sugar (Walz). 100 pts. gratiolin yielded 15·4 gratioletin, 53·5 resin and sugar, which separated from potassio-cupric tartrate a quantity of cuprous oxide equivalent to 28 pts. grape-sugar. According to Walz, the reaction is probably:

$$2C^{40}H^{34}O^{14} = C^{12}H^{12}O^{12} + C^{34}H^{28}O^6 + C^{34}H^{28}O^{10};$$
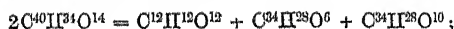
but this equation is not in accordance with the quantities of the decomposition-products actually obtained.—Moreover, gratioletin appears to be formed from gratiolin, merely by elimination of 2HO, not by decomposition (Kr.)—With *oil of vitriol* gratiolin forms a dark red solution, precipitable by water (Walz); slightly (Marchand).—3. When drenched with *nitric acid* of sp. gr. 1·54, it acquires a golden-yellow colour, and then forms a brownish-yellow

solution, which on addition of water, solidifies to a white jelly.—4. It dissolves in caustic *ammonia*, and is precipitated in the gelatinous form by water (Walz). With aqueous ammonia, it turns blue, without dissolving, then quickly becomes white again (Marchand).

Gratiolin is very slightly soluble in *water* (Marchand), in 893 pts. cold and 476 pts. boiling water (Walz). Very soluble in *alcohol*, sparingly in *ether* (Marchand), in 1000 pts. cold and 666 pts. boiling ether (Walz).

Tannate of Gratiolin. —Tannic acid added to an aqueous solution of gratiolin, throws down a dazzling white precipitate easily friable when dry, and insoluble in water (Walz). In presence of a large quantity of ammonia, no precipitate is formed (Marchand).

2. Gratioletin.

Walz. *N. Jahrb. Pharm.* 10, 67.

Comp. p. 467.

Produced, together with sugar and gratiolaretin, by boiling gratiolin with dilute sulphuric acid, and obtained in the preparation of gratiolaretin as already described (p. 466).

Properties. White scales, having a satiny lustre, and exhibiting with the microscope the form of rectangular prisms. At 100° it gives off 3·9 p. c. of (adhering?) water, without further alteration.

						Walz. mean.
34 C	...	....	204	....	65·38	.... 65·14
28 H	....	.. .	28	....	8·97	. ..... 9·12
10 O	.. ... .	....	80	.... ..	25·65	. ..... 25·74

$C^{34}H^{28}O^{10}$ .... 312 .... 100·00 .... 100·00

Appears to differ from gratiolin, $C^{40}H^{34}O^{14}$, only by containing 2 at. HO less (Kr.). ($C^{40}H^{32}O^{12}$, calc. = 65·2 p. c. C. and 8·7 H).

Decomposition. 1. When drenched with *oil of vitriol*, it assumes a yellowish colour, the acid becoming siskin-green, and water added to the liquid throws down white flocks.—2. With *nitric acid* of sp. gr. 1·54, it forms a solution precipitable by water.—3. When evaporated with hydrochloric acid of sp. gr. 1·2, it turns violet and is decolorised by water.—4. It colours *bichromate of potash and sulphuric acid*, green.—5. Not altered by boiling aqueous ammonia, or by potash-ley of sp. gr. 1·22.

Insoluble in *water* and in *ether*, but soluble in *alcohol*.

Appendix to Gratiolin.

1. Gratiosolin.

Walz. *Jahrb. pr. Pharm.* 21, 24 ; 24, 5.—*N. Jahrb. Pharm.* 10, 69.

Gratioline.

Occurs in *Gratiola officinalis*, and is obtained in aqueous solution in the preparation of gratiolin as already described (p. 466). The golden-yellow solution is digested with animal charcoal; the filtrate is evaporated over the water-bath; and the dry residue is freed from traces of gratiolacrin by means of anhydrous ether.

Properties. Amorphous, bright roseate mass, yielding a yellow powder by trituration. Melts at 125°. Has a peculiar odour and a nauseously bitter taste. Permanent in the air.

		at 100°.			Walz (mean).		
					earlier.		*later.*
46	C	276		53·26	....	52·77	.... 53·13
42	H	42		8·12	....	7·86	.... 8·05
25	O	200		38·62	....	39·37	... 38·82
$C^{46}H^{42}O^{25}$		518		100·00	....	100·00	.... 100·00

So, according to Walz, who formerly proposed the formula $C^{18}H^{16}O^{10}$.

Decompositions. 1. Decomposes at 212°.—2. *Burns* when heated with platinum-foil. — 3. In contact with *aqueous acids* or *alkalis*, it is resolved, even at mean temperatures, into sugar and gratiosoletin, both of which remain in solution. According to Walz:

$$2C^{46}H^{42}O^{25} = 2C^{10}H^{34}O^{17} + C^{12}H^{12}O^{12} + 4HO.$$
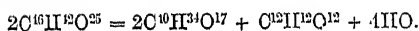
When gratiosolin is heated with acids, the resulting gratiosoletin suffers further decomposition by the action of the acid (see below).—*Oil of vitriol* colours gratiosolin brown-red, the liquid on addition of water yielding a jelly and yellow flocks.—4. Gratiosoletin dissolves in *nitric acid* of sp. gr. 1·54, with evolution of red vapours, and water added to the solution throws down a golden yellow, slightly bitter powder.

Gratiosolin dissolves in 7 pts. cold and 5 pts. boiling *water*, and separates on evaporation, as an oil which gradually solidifies.—It dissolves in *ammonia* with yellow colour; in 3 pts. cold and 2 pts. hot *alcohol*, with golden yellow colour, changing to reddish-yellow on strong concentration. It dissolves slowly in about 1700 pts. of cold and 1100 pts. of boiling *ether*.

2. Gratiosoletin.

WALZ. *N. Jahrb. Pharm.* 10, 70.

Gratiosolin is resolved by contact with acids or alkalis, even at mean temperatures, into sugar and gratiosoletin, which latter may be precipitated by tannic acid. The precipitate is dissolved in alcohol, and decomposed by hydrated oxide of lead, and the filtrate is evaporated, whereupon gratiosoletin remains behind as a golden-yellow very bitter substance.

Calculation according to Walz.				Walz. mean.
40 C	240	......	58·53	58·89
31 H	34	......	8·29	8·27
17 O	136	......	33·18	32·84
$C^{40}H^{31}O^{17}$	410	......	100·00	100·00

Decompositions. 1. By prolonged boiling with dilute *acids*, it is resolved into (38·1 p. c.) sugar and a precipitated mixture of (42·9 p. c.) gratiosoleretin and (10·5 p. c.) hydrogratiosoleretin. According to Walz:—

$$2C^{40}H^{31}O^{17} = C^{12}H^{12}O^{12} + C^{34}H^{26}O^9 + C^{34}H^{28}O^{11} + 2HO.$$
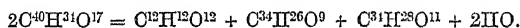
Oil of vitriol dissolves gratiosoletin with red-brown colour, forming sugar and flocks precipitable by water. — 2. With *nitric acid* of sp. gr. 1·54, it forms a dark yellow solution, precipitable by water. — 3. It is decomposed by warm *potash-ley*, with separation of flocks and formation of sugar.

Easily soluble in *water*, in aqueous *ammonia* without alteration, and in ordinary as well as absolute *alcohol;* insoluble in *ether*.

3. Gratiosoleretin.

WALZ. *N. Jahrb. Pharm.* 10, 71.

See page 467.

Gratiosoletin is boiled with dilute sulphuric acid till completely decomposed; the liquid is decanted from the resinous deposit; this deposit is washed with water; and the gratiosoleretin is dissolved out by ether, which leaves hydrogratiosoleretin behind. By evaporating the ethereal solution, indistinct warty masses are at first obtained, and the whole afterwards dries up to a dark yellow powder.

at 100°·				Walz. mean.
34 C	204	......	67·55	67·18
26 H	26	......	8·61	8·71
9 O	72	......	23·84	24·11
$C^{34}H^{26}O^9$	302	......	100·00	100·00

It dissolves in *oil of vitriol*, and is precipitated by a large quantity of water, also in *nitric acid.* — It is not dissolved or decomposed by *hydrochloric acid* or by aqueous ammonia.

Insoluble in *water;* very soluble in *alcohol* and in *ether*.

4. Hydrogratiosoleretin.

WALZ. *N. Jahrb. Pharm.* 10, 71.

See above.

Purified by solution in alcohol and spontaneous *evaporation.*

Pure yellow, amorphous, friable mass, having a faint resinous odour. Melts above 100°.

	at 100°.				Walz. mean.
34 C	204	...	63·75	...	63·67
28 H ...	28	...	8·75	...	8·85
11 O ...	88	...	27·50	...	27·48
$C^{34}H^{28}O^{11}$	320	...	100·00	...	100·00

So, according to Walz. Differs from gratiosoleretin by 2 at. Hl.

At a higher temperature it melts, decomposes, and leaves a combustible cinder. — Dissolves in cold *oil of vitriol*, whence it is precipitated by water, and is carbonised by hot oil of vitriol. — With *nitric acid* of sp. gr. 1·54, it gives off red fumes, and forms a solution precipitable by water. · Nitric acid of sp. gr. 1·2 acts upon it only when heated, forming a yellow resin.

Insoluble in *water*, but dissolves, without colour in cold hydrochloric acid; insoluble in aqueous *ammonia*, but partially soluble in warm potash-ley. Easily soluble in *alcohol*, especially in absolute alcohol, insoluble in *ether*.

5. Gratioloïc Acid.

WALZ.   *N. Jahrb. Pharm.* 10, 79.

Occurs in *Gratiola officinalis.* — In the preparation of gratiolin by the process above-described (p. 466), one of the products obtained is Walz's gratiolacrin, which, according to his more recent statements, may be resolved into gratiola-fat, gratioloïc acid, and brown resins, in the following manner:—The ethereal solution of gratiolacrin, obtained as above (p. 467), is evaporated, and the residue is treated successively with cold absolute alcohol (which partly dissolves the gratiola-fat, partly separates it mechanically), aqueous ammonia, and again with cold alcohol. On boiling the substance then remaining with absolute alcohol, and leaving the solution to cool, crystals of gratioloïc acid are obtained. — This acid may also be obtained from gratiola-fat by the action of potash.

White scales or laminæ, having a satiny lustre and a fatty odour.

					Walz. mean.
28 C	168	...	73·68	...	73·30
28 H	28	...	12·28	...	12·04
4 O	32	...	14·04	...	14·66
$C^{28}H^{28}O^{4}$	228	...	100·00	...	100·00

The above are the numbers deduced by Walz from his analyses; but the analytical data when correctly calculated give 7·46 p. c. hydrogen (Kr.).

6. *Gratiola-fat.* — When the solution of gratiola-fat in absolute alcohol, obtained as above, is precipitated with alcoholic sugar-of-lead, —the resulting precipitate, after being washed with alcohol and suspended therein, decomposed by hydrosulphuric acid,—and the filtrate

mixed with water, drops of oil separate, which do not solidify at mean temperatures, contain 75·12 p. c. C., 11·78 H., and 13·10 O., and consist, according to Walz, of C³¹H²⁸O⁴.

Primary Nucleus C³⁴H³⁴.

Margaric Acid.

$$C^{34}H^{34}O^4 = C^{34}H^{34}, O^4.$$
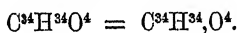
HEINTZ. *Pogg.* 102, 272.

To be distinguished from Chevreul's margaric acid* (p. 357) (*artificial margaric acid*). — Heintz succeeded in preparing this acid; after Köhler and Becker, the former by heating cyanide of potassium with cetylsulphate of potash, the latter by boiling cyanide of cetyl with alcoholic potash, had obtained mixtures of fatty acids from which it was not found possible to separate pure margaric acid (pp. 316, 374).

Preparation. Cyanide of cetyl (oily, prepared as described on page 374) is continuously boiled with alcoholic potash, till ammonia is no longer given off, and the residue has become solid; this residue is then decomposed by boiling dilute hydrochloric acid; the separated fatty acid is shaken up with aqueous ammonia; and the turbid solution is precipitated by chloride of barium. The precipitate, after being washed with water and with alcohol, and repeatedly boiled with ether, yields to this solvent an oil, which solidifies in the cold, melts below 40°, and has the composition of a mixture of cetylic ether and cetylic aldehyde. The undissolved baryta-salt is decomposed by agitation with hydrochloric acid and ether; and by pipetting off the ethereal liquid, and distilling off the ether, crude yellowish margaric acid is obtained, melting at 56·6°, and solidifying in scales and fine needles. This acid may be resolved, by oft-repeated crystallisation from alcohol, repeated partial precipitation from the solution of its soda-salt by acetate of magnesia, and subsequent recrystallisation of the portions of acid again separated (somewhat in the manner described on pp. 210, 211) into margaric acid, and an acid containing a larger proportion of carbon, which occurs chiefly in the portions first precipitated by acetate of magnesia (Heintz).

a. The acid containing the larger amount of carbon is obtained, in small quantity only, even by operating on 98 grms. of cyanide of cetyl, so that, after its melting point has been raised by repeated crystallisation to 62°, no further purification of it is possible. It then solidifies in the scaly crystalline form, contains 76·28 p. c. C., 12·71 H., and 11·01 O., therefore more carbon than stearic acid (76·06 p. c. C., 12·68 H.), and nearly as much as an acid having the formula C³⁸H³⁸O⁴ (76·51 p. c. C., 12·75 H., and 10·74 O.). Its constitution is therefore essentially that which is represented by the latter formula, and it is formed from cyanide of stethyl C³⁶H³⁷Cy, contained in the cyanide of cetyl employed, in the same manner as margaric acid is formed from cyanide of cetyl itself (Heintz).

b. The portions last precipitated by acetate of magnesia yield margaric acid, which, after its melting point has been raised by repeated crystallisation to 59·9°, exhibits the characteristics of a pure

acid, specified on page 210, and cannot in any way be resolved into acids of different melting point.

Properties of Margaric acid. White crystals melting at 59·9°, and solidifying in crystalline scales on cooling.

34 C	204	.... 75·56	.... 75·45	.... 75·55
34 H	34	.... 12·59	.... 12·51	.... 12·57
4 O	32	.... 11·85	.... 12·04	... 11·88
$C^{34}H^{34}O^4$	270	.... 100·00	.... 100·00	.... 100·00

Margarate of Soda. — Obtained like myristate of soda (p. 212).

Margarate of Baryta. — The alcoholic solution of the soda-salt is precipitated with nitrate of baryta, and the precipitate is washed with water. White amorphous powder.

				Heintz.
34 C	204·0	.... 60·44	.... 60·39
33 H	33·0	.... 9·78	.... 9·80
3 O	24·0	.... 7·11	.... 7·41
BaO	76·5	.... 22·67	..... 22·40
$C^{34}H^{33}BaO^4$	337·5	... ... 100·00	.... 100·00

Margarate of Silver. — Thrown down from the soda-salt by nitrate of silver, as a faint grey precipitate, which dries up to a loose, white, amorphous powder.

				Heintz.
34 C	204	.... 54·11	.... 53·67
33 H	33	.... 8·75	.... 8·74
4 O	32	.... 8·49	.... 8·74
Ag	108	.... 28·65	.... 28·85
$C^{34}H^{33}AgO^4$	377	.... 100·00	.... 100·29

Margaric and Myristic Acids. — Mixtures of these acids are mostly opaque, uncrystalline, and exhibit the following melting points:—

A mixture of—		Melts at	Mode of Solidifying.
Margaric acid.	Myristic acid.		
90	10	57·5°	Scaly-crystalline, not very distinct.
80	20	55·5°	Indistinctly crystalline.
70	30	53·5°	Almost wholly uncrystalline, with tolerably even surface.
60	40	50·5°	Amorphous, opaque.
50	50	46·2°	The same.
40	60	45·6°	Somewhat granulo-crystalline.
30	70	44·7°	Similar, with larger grains intermixed.
20	80	43·8°	Similar : grains very indistinct.
10	90	51·8°	Opaque; in scarcely perceptible concentric needles.

Margaric and Palmitic Acids. — The mixtures solidify partly like the pure acids — those containing 80 or 90 p. c. palmitic acid, in beautiful long needles, just like the mixture of stearic and palmitic acids formerly called margaric acid.

| A mixture of— | | Melts at | Mode of Solidifying. |
Margaric acid.	Palmitic acid.		
90	10	58·7°	Scaly-crystalline.
80	20	57 6°	Similar, but somewhat flowery.
70	30	56·9°	Like the preceding mixture.
60	40	56·5°	The same.
50	50	56·0°	The same.
40	60	56·0°	The same.
30	70	57·0°	Very beautifully flowery, almost in long needles.
20	80	58·6°	In long needles.
10	90	60·2°	The same.

Oxygen-nucleus $C^{34}H^{32}O^2$.

Roccellic Acid.

$$C^{34}H^{32}O^8 = C^{34}H^{32}O^2,O^6.$$
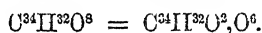
Fr. Heeren. *Schw.* 59, 346.
Liebig. *Pogg.* 21, 31.
Schunck. *J. pr. Chem.* 38, 459; *Ann. Pharm.* 61, 78; *Phil. Mag. J.*, 29, 261.
Hesse. *Ann. Pharm.* 117, 332.

Discovered in 1830 by Heeren; investigated especially by Hesse.

Occurrences. In *Roccella fuciformis.* Ach. According to Heeren, also in *Lecanora tartarea.*

Preparation. 1. *Roccella tinctoria* is exhausted with aqueous ammonia; the filtrate is precipitated by chloride of calcium; the well washed precipitate is decomposed by hydrochloric acid; and the acid thus separated is purified by solution in ether (Heeren). The liquid filtered from the roccellate of lime retains erythric acid (xii, 381) in solution. — 2. The lichen is freed from erythric acid by milk of lime; the residue is boiled with dilute hydrochloric acid; the acid solution is removed; and the residue warmed with dilute soda-ley. From the greenish-brown solution, hydrochloric acid throws down green flocks, which must be suspended in water and treated for a short time with chlorine gas, which chiefly removes the green substances. The acid, after being treated with chlorine, is washed with water, and purified by recrystallisation

from boiling alcohol, with help of animal charcoal (Hesse). The acid obtained by method 1, may also be purified in this manner, or by passing chlorine into the alkaline solution (Hesse). — 3. The lichens are exhausted with ether in a percolator; the ether is distilled off; and the greenish white crystalline residue is dissolved in the smallest possible quantity of borax-solution, a portion then separating out as the liquid cools. The rest is precipitated by hydrochloric acid, and purified by re-solution in boiling aqueous borax, then, together with the portion of acid first obtained, by recrystallisation from ether, with help of animal charcoal (Hesse). — Schunck treats the lichens exhausted with boiling water, and thereby freed from erythric acid [and picroerythrin (xii, 30)], with boiling alcohol; separates the green flocks which fall down as the tincture cools; and evaporates the filtrate to dryness. From the residue, boiling water extracts a small quantity of picroerythrin; the solution then prepared with cold alcohol deposits, on addition of alcoholic sugar-of-lead, greenish white flocks of roccellate of lead, which are decomposed with nitric acid; and the acid thus separated is purified by recrystallisation from boiling alcohol, with help of animal charcoal.

Properties. Delicate, white, rectangular, four-sided plates, having a silvery lustre; from alcohol it separates in short needles. Melts at about 130°, without loss of weight, and solidifies again on cooling to a white crystalline mass (Heeren). Melts at 132° to a colourless liquid, which solidifies in the crystalline form at about 108°. At a temperature somewhat below 200°, a portion volatilises, while another portion is converted into an anhydride (Hesse). Tasteless and scentless; the alcoholic solution has an acid reaction.

					Liebig.		Schunck.		Hesse.
					mean.		*mean.*		*mean.*
34 C	.....	204	.....	68·00	.....	67·03	..... 65·95	.....	67·9
32 H	.....	32	.....	10·66	.....	10·75	..... 10·67	.....	10·6
8 O	.....	64	.....	21·34	.....	22·22	..... 23·38	.....	21·5
$C^{34}H^{32}O^8$	.....	300	.....	100·00	.....	100·00	..... 100·00	.....	100·0

The formulæ $C^{16}H^{16}O^4$ (Liebig), $C^{26}H^{24}O^6$ (Kane, *Phil. Trans.* 1840, 299), $C^{34}H^{36}O^6$ (Schunck) were successively adopted for roccellic acid, till Hesse established the above. — The acid belongs to the oxalic series, and is therefore homologous with oxalic, sebacic acid, &c. (Hesse).

Decompositions. 1. Roccellic acid heated to between 220° and 280°, gives off water, turns brown, and forms roccellic anhydride (Hesse). *By dry distillation* it yields, products similar to those obtained from the fats, and having a sharp irritating taste (Heeren); it yields a distillate which solidifies in the crystalline form, and after repeated distillation, remains oily, leaving little or no residue (Schunck). — 2. Heated on platinum foil, it melts, gives off a fatty odour, and *burns* with a bright flame, leaving no residue (Heeren, Schunck). — 3. The soda-salt is not altered by the passage of an *electric current* (Hesse). — 4. The acid is not decomposed by *bromine*, even in sunshine. — 5. With anhydrous *sulphuric acid*, it carbonises without emission of gas; dissolves with brown colour in fuming sulphuric acid, and is not decomposed by oil of vitriol. — 6. *Hydrochloric acid* does not act on roccellic acid; a mixture of hydrochloric acid and chlorate of potash decomposes it only after long boiling. — 7. From solution in boiling

fuming nitric acid, roccellic acid crystallises on cooling, for the most part unaltered; but by prolonged boiling the roccellic acid is decomposed, and volatile acids having the odour of butyric acid are given off, but no crystallisable non-volatile acids are produced. — 8. Roccellic acid heated with *hydrate of potash*, froths violently at 260°, and gives off a small quantity of oil. The residue contains neither volatile acids nor oxalic acid, but a large quantity of unaltered roccellic acid (Hesse). — 9. The alcoholic solution of roccellic acid does, not reduce *terchloride of gold*, even at the boiling heat (Schunck). — 10. The acid heated with *aniline* forms roccellanilide (Hesse).

Combinations. The acid is perfectly insoluble in *water*, not dissolving even in 100,000 pts. at the boiling heat (Heeren).

With the alkalis, it forms soluble salts; with other bases, for the most part, insoluble *bimetallic salts* $C^{34}H^{30}M^2O^4$. The acid dissolves in aqueous borax, phosphate of soda, and roccellate of soda (Hesse). It expels carbonic acid from alkaline carbonates (Schunck).

Roccellate of Ammonia. — The residue left on evaporating the ammoniacal solution is amorphous and brittle. According to Heeren, it dissolves very easily in water, forming a frothy liquid, which in the concentrated state, takes up an additional quantity of acid, and gives it up again on dilution with water. According to Hesse, it is decomposed by drenching with water, with separation of a white jelly.

Roccellate of Potash. — The acid dissolves readily in alcoholic potash, swells up when drenched with strong potash-ley, and dissolves only on addition of water (Hesse). Delicate crystalline laminæ having a fatty lustre, and dissolving to a frothy liquid (Heeren, Hesse).

Roccellate of Soda. — From a solution of roccellic acid in dilute soda-ley, a strong solution of soda throws down white flat needles of the soda-salt (Hesse).

Roccellate of Baryta. — From an ammoniacal solution of roccellic acid, chloride of barium throws down a bulky white precipitate, which soon becomes dense, and exhibits a silky lustre when dry. — It is somewhat soluble in boiling water, insoluble in pure alcohol, but easily soluble in alcohol containing acetic acid (Hesse).

		at 100°.'				Hesse.
34 C	.....	204·0	......	46·87	......	46·0
30 H	.....	30·0	......	6·89	......	6·9
2 Ba	.....	137·2	......	31·52	......	31·5
8 O	.....	64·0	......	14·72	......	15·6
$C^{34}H^{30}Ba^2O^8$	.....	435·2	......	100·00	......	100·0

Roccellate of Lime. — The ammoniacal salt is precipitated by chloride of calcium, and the white amorphous precipitate is washed with water and with alcohol. It gives off 48 p. c. water at 160°, and at a higher temperature vapours of acrolein and a combustible gas (Hesse).

						Hesse.
$C^{34}H^{30}O^8$	.....	298	......	83·71	..... .	
2 Ca	.....	40	......	11·24	..... .	11·1
2 HO	.....	18	......	5·05	..... .	4·8
$C^{34}H^{30}Ca^2O^8$ + 2aq	.....	356	......	100·00	......	

Roccellate of Magnesia. — When roccellate of ammonia is mixed with aqueous sulphate of magnesia, the mixture becomes turbid, from separation of a small quantity of the free acid. On heating the clear filtrate to 38°, drops of oil separate from it, but the liquid becomes clear again on cooling ; after prolonged boiling, it yields an amorphous precipitate, probably of free roccellic acid, which does not redissolve (Hesse).

Roccellate of Zinc. — Obtained by double decomposition as a white amorphous precipitate, soluble in aqueous ammonia, insoluble in water and in alcohol (Hesse).

Roccellate of Lead. — *Basic.* — Precipitated from roccellate of ammonia by neutral acetate of lead (Schunck). An alcoholic solution of roccellic acid forms, with a warm alcoholic solution of neutral acetate of lead, a white precipitate which must be washed with alcohol. White powder, which gives off a small quantity of water at 100°, then 3·8 p. c. at 125°, baking together at the same time, and melts at a higher temperature (3 at. water = 4·1 p. c.) (Hesse).

			at 100°.				Hesse.	Schunck.
34	C		201 0	....	31·67	....	31·6	... 34·02
33	H		33 0	....	5·12	....	4·7	... 5·14
3	Pb		311 1	....	48·30	....	48·3	.... 47·56
12	O		96 0	....	14·91	....	15·4	.... 13·28
$C^{34}H^{30}Pb^2O^8,PbO,3HO$			644·1	....	100·00	....	100·0	... 100·00

Roccellate of Silver. — The ammonia-salt is precipitated by nitrate of silver, and the precipitate is boiled with alcohol, to remove free acid. — White amorphous mass, which turns grey on exposure to light, and when strongly heated, yields at first a nearly colourless distillate and suffocating white vapours, afterwards a brown distillate (Hesse).

			Hesse.
$C^{34}H^{30}O^8$	298	.... 57·98	....
2Ag	216	.... 42·02	.... 41 to 41·6
$C^{34}H^{30}Ag^2O^8$	514	.... 100·00	

Roccellic acid dissolves in 1·81 pts. boiling *alcohol* of sp. gr. 0·819. Easily soluble in *ether* (Heeren). Slightly soluble in warm *benzol* (Hesse).

Oxygen-nucleus $C^{34}H^{30}O^4$.

Roccellic Anhydride.

$$C^{34}H^{30}O^6 = C^{34}H^{30}O^4,O^2.$$
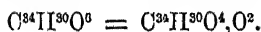
HESSE. *Ann. Pharm.* 117, 340.

Roccellic acid is heated in an oil-bath to at least 220° ; the fused brown mass is mixed with dilute soda-solution till it acquires an alkaline reaction, then shaken up with ether ; and the ethereal layer is decanted and evaporated, the anhydride then remaining.

Colourless or faintly yellow neutral oil having a fatty odour. Makes grease-spots on paper.

|		at 100°.			Hesse.
34 C	....	204	......	72·34	...... 72·0
30 H	....	30	......	10·64	.... 10·8
6 O	....	48	....	17·02	.... 17·2
$C^{34}H^{30}O^6$	....	282	....	100·00	...... 100·0

Boiling *soda-ley* converts it into roccellic acid.—The solution in warm *ammonia-water* mixed with hydrochloric acid, deposits white flocks easily soluble in alcohol, and remaining, when the alcohol is evaporated, as a semi-crystalline acid oil having a burning taste, probably a mixture of roccellic and roccellamic acids.

The anhydride is sparingly soluble in cold, easily soluble in hot *alcohol* and in *ether*.

Roccellate of Ethyl.

$$C^{42}H^{40}O^8 = 2C^4H^5O, C^{34}H^{30}O^6.$$
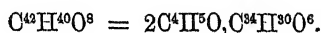
HESSE.   *Ann. Pharm.* 117, 340.

Roccellic ether.

Roccellic acid is dissolved in warm alcohol; hydrochloric acid gas is passed into the liquid; the alcohol is removed after a few hours; and the oil which separates is washed with alkaline and with pure water, then dried over oil of vitriol.

Pale yellow oil having a faint aromatic odour. Lighter than water. —Insoluble in *water* and in aqueous *ammonia*, and not attacked either by aqueous or by alcoholic ammonia, even after several months' contact or when heated to 118°.—Easily soluble in *alcohol*, less easily in *ether*.

		Over oil of vitriol.			Hesse.
42 C	....	252	....	70·79	.... 71·0
40 H	....	40	....	11·24	.... 11·3
8 O	....	64	....	17·97	.... 17·7
$2C^4H^5O, C^{34}H^{30}O^6$	....	356	....	100·00	.... 100·0

Roccellanilide.

$$C^{58}N^2H^{42}O^4 = 2C^{12}NH^7, C^{34}H^{28}O^4.$$
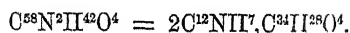
HESSE.   *Ann. Pharm.* 117, 342.

Roccellphenylamide.

When roccellic acid is heated with excess of aniline to 180°—200°, water and aniline distil over, and a black pitchy residue is left, which when drenched with alcohol yields crystals after a few days. These

are collected and purified by repeated crystallisation from boiling alcohol, with help of animal charcoal.

Beautiful colourless laminæ, which melt to a colourless liquid at 53·3° and solidify partially at 52°. Neutral. — At a somewhat elevated temperature, it yields a colourless distillate, without any carbonaceous residue.
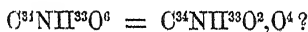
		Over oil of vitriol.		Hesse.
58	C	348	77·33	76·9
42	H	42	9·33	9·8
2	N	28	6·22	
4	O	32	7·12	
$C^{58}N^2H^{42}O^4$		450	100·00	

Insoluble in *water*, aqueous *ammonia*, and *hydrochloric acid*. Not coloured by *hypochlorite of soda*. The alcoholic solution does not precipitate alcoholic *neutral acetate of lead*.

Primary Nucleus $C^{34}H^{36}$; *Oxyazo-nucleus* $C^{34}NH^{33}O^2$.

Cerebrin.

$$C^{34}NH^{33}O^6 = C^{34}NH^{33}O^2,O^4?$$

VAUQUELIN. *Ann. Chim.* 81, 37, and 60; *Schw.* 8, 430.
L. GMELIN. *Tiedemann's Zeitschr. f. Physiol.* 1, 122.
COUERBE. *Ann. Chim. Phys.* 56, 164; *Ann. Pharm.* 40, 75.
ED. FRÉMY. *J. Pharm.* 27, 457; *N. Ann. Chim. Phys.* 2, 463; *Ann. Pharm.* 40, 75.
GOBLEY. *N. J. Pharm.* 9, 1, 83, and 161; 11, 409; 12, 5; 17, 401; 18, 107; 19, 406; 21, 241; 30, 241; 33, 161.
v. BIBRA. *Vergleich. Unters. über das Gehirn der Menschen u. d. Wirbelthiere.* Mannheim, 1854; abstr. *Ann. Pharm.* 105, 368.
W. MÜLLER. *Ann. Pharm.* 103, 131; 105, 379.

Cerebrate (Couerbe): *Cerebric acid* (Frémy). Under the names *Brain-fat, phosphoretted Bile-fat* and *Cerebrin*, there were described, in the third edition of this Handbook, according to Fourcroy, Vauquelin, and others, laminæ of an unsaponifiable substance, melting at 136°, easily soluble in ether, and giving off 5·4 p. c. water when heated: doubtless therefore a mixture consisting chiefly of cholesterin. The body described in the same place as *brain-wax* [according to Gmelin] agrees more closely with that which is now called cerebrin.

Occurrence. In the brain. In the fat of the spinal marrow and nerves (Frémy; v. Bibra). — It is a constituent of the viscous matter (see below) obtained from yolk of egg, the eggs of the carp, the milt or soft roe of the carp and herring, the fat of venous blood, ox-bile and vineyard-snails, and separates in grey films when this substance is decomposed by acids, or in white films when it is decomposed by alkalis (Gobley).

Preparation. When brain (of oxen) is triturated with water to a thin milk, and the emulsion thus obtained is mixed with solution of

neutral acetate of lead, till it separates after a while into an upper, clear, blood-red layer, and an under-layer containing the brain-pulp, the liquid, if heated to the boiling-point after it has stood for twelve hours and the sediment has been uniformly comminuted, deposits greyish-red flocks, itself at the same time becoming clear and easy to filter. The liquid which runs through contains uric acid, inosite, creatine, and other matters, and the separated coagulum contains cerebrin, liquid and solid substances, and cholesterin.

The expressed coagulum is exhausted, first by treatment with hot alcohol, then by boiling with ether-alcohol, filtered at the boiling heat and left to cool; it then deposits a large quantity of white flocks, which contain cerebrin, cholesterin, and fats, and dry up to a reddish-yellow, crystalline mass. The other fats remain dissolved in the alcohol. The precipitate is collected, dried, freed from cholesterin and brain-fat by repeated exhaustion with cold ether, and dissolved in boiling alcohol, which, on cooling, deposits the cerebrin, to be purified by repeated crystallisation from boiling alcohol (W. Müller).

When brain is beaten up with baryta-water to a milk, and the mixture is heated to boiling, cerebrin may also be separated from the resulting coagulum in the manner just described (W. Müller). — v. Bibra mixes the extract of brain prepared with boiling alcohol, and the fat which separates from it on cooling, with potash-ley, and boils for several hours; the solution then becomes darker-coloured and clear, and after standing in the cold for 24 hours, deposits nearly all the cerebrin. This substance may also be obtained by successive and repeated treatment with hydrochloric acid and potash-ley, and finally purified with hydrochloric acid.

Frémy treats comminuted brain repeatedly with boiling alcohol, and leaves it for some days in contact with the alcohol, which coagulates the albumin, dehydrates the brain, and thereby renders it accessible to the subsequent treatment with ether. It is then pressed, quickly triturated in a mortar, and treated successively with cold and with warm ether. The ether is evaporated, and the extract redissolved in a large quantity of ether, whereupon cerebrin is deposited in the form of a white powder. It still, however, retains lime and soda-salts, together with oleophosphoric acid and albumin, to remove which the precipitate is redissolved in boiling absolute alcohol containing sulphuric acid. The mixture of oleophosphoric acid and cerebrin, which separates as the liquid cools, is freed from oleophosphoric acid by washing with cold ether, and recrystallised from boiling ether. The alcohol which has been boiled with the brain likewise deposits cerebrin on cooling, while fats remain in solution (Frémy).

Couerbe comminutes brain, after it has been washed and freed from membranes, and exhausts it by four successive treatments with cold ether, which first displaces the water from the brain, and then takes up the fats and cholesterin. The residue is repeatedly exhausted with boiling alcohol of 40°, as long as the solutions yield deposits on cooling. The deposits are collected and washed with cold ether, which takes up cholesterin and leaves cerebrin undissolved. The alcoholic extracts, when concentrated, deposit at first an additional quantity of cerebrin, till a semi-fluid fat makes its appearance, which dissolves in ether, and separates again in the form of an oil. — The ethereal extract still retains cerebrin, which, after the evaporation of the ether, sometimes remains undissolved on treating the residue with small

quantities of ether, and may then be separated by filtration. In either case, the residue redissolves completely in ether, and may then, according to Couerbe, be resolved into *cephalote, stearoconote, eleencephol*, cerebrin, and cholesterin. — On the three substances just mentioned, which, however, must, in all probability, be still regarded as mixtures, see Couerbe (*loc. cit.*), Frémy (*J. Pharm.* 27, 472), *Ann. Pharm.* 40, 88), also Simon (*J. pr. Chem.* 20, 271), Berzelius (*Pogg.* 41, 412).

From the viscous matter of yolk of egg, &c. 200 grms. of the viscous matter are drenched with 500 grms. alcohol, of 88 p. c., and 50 grms. hydrochloric or sulphuric acid ; the whole, after standing a few hours, is heated to boiling ; and the oily layer which rises to the surface on cooling, is removed. The alcoholic solution, when left to itself, deposits a mixture of cerebrin and cholesterin, which is collected, spread out on paper to absorb the fat, freed from obstinately adhering acid by repeated solution in boiling alcohol, from cholesterin by washing with ether, and again crystallised from boiling alcohol. It then still retains phosphate of lime, which can be removed only by repeated solution in alcohol. If the cerebrin separates on cooling together with the oil, the mixture must be collected on a filter, and the cholesterin and oil removed by ether (Gobley).

Properties. White, loose, very light powder, appearing under the microscope in the form of rounded grains (Müller). Small, white, apparently crystalline grains, which bake together on drying ; it mostly takes the form of soft, waxy laminæ (Gobley). According to Frémy, it is granulo-crystalline. Does not give off any water at 75° (Müller). Changes, on drying, to a translucent, friable wax (Couerbe). Infusible (Couerbe) ; does not melt till it begins to decompose (Frémy ; v. Bibra) ; in the hydrated state it melts at a gentle heat ; after drying, between 155° and 160° ; more easily in presence of water or fat (Gobley). See below. — Tasteless and scentless. Neutral. Lighter than water. Does not make grease-spots on paper.

					Couerbe.	Frémy.
34 C	....	204	....	68·23	.... 66·90	66·7
N	....	14	....	4·68	.... 3·40	2·3
33 H	....	33	....	11·04	.... 11·10	10·6
6 O	....	48	....	16·05	.... 16·27	19·5
P	....				2·33	0·9
$C^{34}NH^{33}O^6$	....	299	....	100·00	... .. 100·00	100·0

		Thomson.		Gobley.		v. Bibra.		Müller.
34 C	....	67·04	....	66·85	....	67·01	.... 66·80	68·45
N	....	2·24	....	2·29	....	2·10	.... 2·51	4·61
33 H	....	10·85	....	10·82	....	10·75	.... 10·65	11·27
6 O	....	19·41	....	19·61	....	19·72	.... 19·52	15·67
P	....	0·46	....	0·43	....	0·42	.... 0·52	
$C^{34}NH^{33}O^6$	....	100·00	....	100·00	....	100·00	.... 100·00	100·00

Gobley analysed cerebrin dried at 120° (see below) : *a* from yolk of egg ; *b* from carp-milt ; the cerebrin of the other analysts was obtained from brain. — Couerbe's cerebrin contained 2·14 p. c. sulphur, unless indeed he mistook phosphate of baryta for sulphate. Müller first succeeded in separating the phosphorus, which had previously been regarded as an essential constituent of the brain, although Gobley had already found that cerebrin containing phosphorus left, when burnt, phosphate of lime not

exhibiting any acid reaction. — The fable that cerebrin from the brains of idiots contains very little phosphorus, while that of sane or of deranged individuals contains a larger quantity, is of Couerbe's invention. See Lassaigne (*J. Chim. méd.* 11, 344).

Decompositions. 1. Müller's cerebrin decomposes, when heated to 80°, assuming a yellow-brown colour; Gobley's requires a heat of 160° to turn it brown and decompose it; Vauquelin's melts at 175° to a brown viscid liquid, which solidifies in the form of a resin — 2. When heated on platinum-foil, it turns brown, gives off the odour of burnt horn; then melts and burns with a red flame, leaving a perfectly combustible cinder (Müller). — 3. It is not altered by cold concentrated *nitric* acid, but when heated therewith, it swells up, eliminating red vapours, froths strongly, and deliquesces, at commencing ebullition, to a yellow transparent oil, which for a while undergoes no further alteration. This oil solidifies on cooling to a yellowish white fat; after being purified by washing with water, and dissolved in boiling alcohol, it is deposited in the course of 24 hours in white grains, which, when examined by the microscope, are seen to consist of drops of fat, without a trace of crystallisation. It contains 75·52 p. c. carbon, and 12·92 hydrogen; has a slight acid reaction, melts on platinum foil, burns with a fatty odour, and dissolves in cold alcohol and ether (Müller). — 4. With cold *oil of vitriol*, cerebrin forms a dark purple-red solution, which is decolorised by water, with precipitation of yellow tenacious flocks (Müller). The solution turns black on standing. An excess of warm dilute sulphuric acid forms with cerebrin a black pulp, which, when largely diluted with water, leaves on the filter a tough brown resin (v. Bibra). — 5. Cerebrin remains unaltered in cold *hydrochloric* (and *phosphoric*) *acid*, acquires a reddish-violet colour in the boiling acid, but is not completely decomposed till after long boiling (v. Bibra), the liquid at the same time becoming brown, and depositing a brown resin, insoluble in acids and in alkalis (Müller). — 6. With fresh bile, water, and oil of vitriol, cerebrin exhibits the same red colouring that is produced under similar circumstances by grape-sugar (v. Bibra, xv, 322).

Combinations. Cerebrin is not altered in cold *water*, but swells in boiling water like starch, and forms a thin, easily clouded solution, which froths like soap-water, does not alter on cooling, and leaves unaltered cerebrin when evaporated (Müller). Gobley and Frémy do not regard the liquid obtained with boiling water as a peculiar solution. — According to Gobley, cerebrin unites with *mineral acids*, or retains them obstinately.

Cerebrin is not saponifiable (Vauquelin, Couerbe). It does not form salts with bases (Gobley, v. Bibra, Müller). This statement is opposed to that of Frémy, who regards cerebrin as an acid. Cerebrin is not dissolved by aqueous ammonia, potash, or soda, even with the aid of heat (Frémy, Müller), but it takes up a portion of these bases (Frémy). From alcohol containing potash it takes up the alkali, but in quantity varying according to the concentration and temperature of the solution, and the time during which the resulting compound is washed with alcohol (Gobley). From an alcoholic solution of cerebrin, potash, soda, and ammonia throw down precipitates insoluble in alcohol. The precipitate formed by potash-ley dissolves partially on further boiling, and the undissolved portion yields cerebrin to boiling alcohol,

while a small portion of yellow resin remains behind. Baryta-water behaves with cerebrin in the same manner as potash-ley, not forming a cerebrate of baryta (such as Frémy thought he had obtained by boiling cerebrin with water and excess of baryta) (Müller).

Cerebrin dissolves in boiling *alcohol* and *ether* (Müller). It requires a large quantity of boiling alcohol of 88 p. c. to dissolve it, and separates on cooling, for the most part, in a very bulky form, but dissolves easily in absolute alcohol, not in ether (Gobley).

Appendix to Cerebrin.

Phosphoretted Fats.

Vauquelin (*Ann. Chim.* 81, 37, and 60) first directed attention to the occurrence of a phosphoretted fat in the human brain. Similar fats were afterwards examined by Frémy, Gobley, and others, with very varying results, not one of them having been obtained in a state of purity.

a. Frémy's *Oleophosphoric acid.* — When the ethereal extract of brain, prepared as above described (p. 480), is treated with ether to separate cerebrin, the ether takes up oleophosphoric acid, often combined with soda, and mixed with olein and cholesterin. The ethereal solution is evaporated; the soda is extracted by an acid; the residue is dissolved in boiling alcohol; and the solution is left to cool, the oleophosphoric acid being then deposited. The olein and cholesterin still mixed with it may be removed, though not completely, by absolute alcohol. — Oleophosphoric acid thus obtained is gummy, generally yellow, and contains from 1·9 to 2·0 p. c. phosphorus. When burnt in contact with the air, it leaves a carbonaceous mass containing phosphoric acid. By long boiling with water or alcohol, more quickly with acidulated water, it gradually loses its viscosity, and is converted into perfectly pure olein (containing 78·87 p. c. C., 11·98 H., and 9·15 O.), while the lower stratum of liquid is rendered strongly acid by the phosphoric acid produced. The same decomposition takes place very slowly at ordinary temperatures; also at the commencement of putrefaction of the brain. Fuming nitric acid decomposes oleophosphoric acid into phosphoric acid and a fatty acid. Alkalis in excess form a phosphate, an oleate, and glycerin. — The acid is insoluble in water, but swells up slightly in boiling water. With ammonia, potash, and soda, it immediately forms soapy compounds, with the other bases, insoluble salts. It is insoluble in cold absolute alcohol, easily soluble in boiling alcohol and in ether (Frémy, *J. Pharm.* 27, 463 ; *N. Ann. Chim. Phys.* 2. 474 ; *Ann. Pharm.* 40, 79). The muscles of vertebrate animals, shaken up with cold weak alcohol, yield to that liquid a viscid, ambergris-coloured substance, which dissolves but imperfectly in water, and when treated with sulphuric acid, is resolved into sulphate of soda and oleophosphoric acid. Oleophosphate of soda occurs in almost all parts of the animal body, its quantity increasing with the age of the animal, and differing in amount in different species of vertebrate animals. Fishes with white light flesh (such as the whiting, sole, and plaice) contain but small quantities of it, whereas larger quantities are found in the herring, salmon, mackerel, salmon-

trout, and other fishes with firmer flesh (Valenciennes & Frémy, *N. Ann. Chim. Phys.* 50, 172).

The yolk of the eggs of cartilaginous fishes contains a fat soluble in alcohol and ether, which forms a gum with water, and resembles oleophosphoric acid. Phosphoretted fats are also found both in the slightly developed and in the ripe eggs of cartilaginous fishes, and in the eggs of adders (Valenciennes & Frémy). — By pressing the muscles of salmon, a red oil is obtained, which, when shaken up with alcohol containing ammonia, loses its colour, and gives up to the liquid a red colouring matter, which is precipitated as a tenacious mass by acids. Whether this mass, the *Acide salmonique* of Valenciennes and Frémy belongs to this place, there are not sufficient data to determine.

b. *Müller's Phosphoretted Brain-fat.* — When the alcoholic brain extracts obtained in the preparation of cerebrin (p. 480) have deposited the cerebrin and cholesterin, and are then mixed with the mother-liquors obtained in the purification of the cerebrin, and the united solutions are boiled with hydrated oxide of lead, the fatty acids are precipitated in the form of lead-salts. These salts are separated by repeated treatment with ether, into a solution and a portion insoluble in ether (also in water and in alcohol), and this latter portion, when decomposed by hydrosulphuric acid, yields an acid oil and pearly scales free from phosphorus. — The ethereal solution leaves, on evaporation, a reddish-yellow waxy lead-salt, a portion of which is taken up by boiling alcohol. This portion, when recrystallised, is white, finely pulverulent, and turns brown at 70°. When the portion of the lead-salts extracted by ether, which is insoluble in boiling alcohol, is again treated with ether, a small quantity of yellowish powder is left behind, while the greater part dissolves, with dark red colour. On evaporating this (alkaline) solution, there remains a brittle, red-brown, easily friable lead-salt, which is not altered even by repeated solution in ether and evaporation, and exhibits the following relations : It varies in composition, containing from 28·26 to 29·7 p. c. carbon, 4·19 to 4·31 hydrogen, 3·72 phosphorus, 42·86 to 45·17 lead, and is free from nitrogen. It is insoluble in water, also in alcohol, whether cold or boiling. When decomposed under alcohol by hydrosulphuric acid, it yields an acid alcoholic solution, which on standing deposits a red-brown tenaceous acid mass, and forms yellow flocks with baryta-water. These flocks, which are friable when dry, contain phosphorus and 32·81 p. c. barium, and are insoluble in water, alcohol, and ether (Müller, *Ann. Pharm.* 105, 379).

c. Gobley's *Matière visqueuse* and *Lecithin.* A constituent of yolk of egg, resembling ear-wax, described by Kodweiss (*Ann. Pharm.* 59, 261), agrees in properties with the substance described by Gobley.

The eggs and milt or soft roe of the carp (and herring); the yolk of poultry-eggs, the brain of the domestic fowl (of man and of the sheep), venous blood, ox-bile, and the fat of the vineyard snail, contain, together with cholesterin, olein and margarin, a viscous substance which is decomposed by boiling with acidulated water, yielding cerebrin, oleic acid, margaric acid and phosphoglyceric acid (ix, 492). Of these products, Gobley regards the cerebrin as adventitious, the other three as resulting from the decomposition of a non-isolable substance, *lecithin.* — The portion of pig's bile soluble in alcohol and not precipitable by ether, contains, besides cholesterin and ordinary fats, a

phosphoretted fat corresponding with Gobley's lecithin, and resolvable by boiling with baryta-water into phosphoglycerate of baryta and insoluble baryta-salts (Ad. Strecker, *Ann. Pharm.* 123, 359).
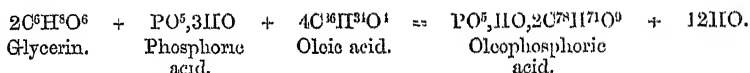
When carps' eggs are exhausted with ether or boiling alcohol, and the solution is evaporated, there remains a reddish-yellow soft mass, which when redissolved in boiling alcohol, leaves a small quantity of oil, and separates again as a viscous mass on cooling. — It may also be obtained in the same manner, but less pure, from yolk of egg (xi, 493) — When the comminuted and partially dried milt of the carp is shaken up with ether, the ether takes the greater part of the viscous matter, and the rest may be obtained by repeated boiling with alcohol. On evaporating the alcoholic solution, transferring the viscous matter contained in the residue to ether by agitation therewith, and evaporating the ether, the viscous matter is obtained free from the salts taken up by the alcohol, which remain in the lower watery layer of liquid. The viscous matter is colourless, or has merely a faint yellow or orange tint, it is soft, neutral, and has for the most part the odour of the material from which it has been prepared. It is frequently contaminated with earthy phosphates and albumin.

It swells up when *heated*, chars without melting, gives off ammoniacal vapours, and leaves an acid carbonaceous residue containing phosphoric acid. — When exposed to the *air*, it does not turn acid, and afterwards yields the same decomposition-products as that which has been prepared without exposure to the air. — When shaken up with *water*, it forms an emulsion which does not become sour or exhibit the presence of phosphoglyceric acid, even after 12 hours' boiling, but on boiling it with water containing *sulphuric* or *hydrochloric acid*, oleic and margaric acids are formed, which rise to the surface as an oil, and phosphoglyceric acid which remains dissolved in the water. Addition of alcohol accelerates this decomposition, which, in viscous matter from yolk of egg, takes place at the mere heat of the water-bath, but in that derived from other sources, not till after half an hour's actual boiling. The oxygen of the air has no influence on the decomposition. Besides the products above mentioned, there are obtained cerebrin, and sometimes also cholesterin, olein and margarin, which however are regarded by Gobley as accidental admixtures. — Aqueous *alkalis* and *alkaline carbonates* at the boiling heat produce the same decomposition as the mineral acids. When the viscous matter of yolk of egg is shaken up with water containing potash and heated in the water-bath, acetic acid separates oleic and margaric acids from it; with the viscous matter of the brain or from any other source, boiling with alcoholic potash is necessary to effect the decomposition. Carbonate of potash also does not decompose the viscous matter merely at the heat of the water-bath, but only on actual boiling. — Six hours' boiling with *acetic* (lactic or tartaric) acid does not produce any decomposition, 12 hours' boiling only an imperfect decomposition of the viscous matter; but by 24 hours' boiling, it is completely decomposed, with formation of phosphoric acid and glycerin (Gobley).

From the emulsion formed by *water*, which froths like soap (Gobley), it is precipitated by common salt (Kodweiss).

The viscous matter dissolves sparingly in cold, easily in boiling *alcohol*; it is also soluble in ether (Gobley). See references given under *Cerebrin* (p. 479).

Berthelot (*Chim. organ.* 2, 46 and 81) designates oleophosphoric acid as *Acide glycéroléophosphorique* or *glycéromargaroléophosphorique*, and regards it as a monobasic acid formed from 2 at. glycerin, 1 at. phosphoric acid and 4 at. oleic or margaric acid, with elimination of 12 at. water:
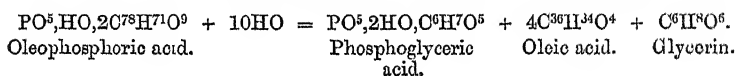
$$2C^6H^8O^6 + PO^5,3HO + 4C^{36}H^{34}O^4 = PO^5,HO,2C^{78}H^{71}O^9 + 12HO.$$

Glycerin.   Phosphoric acid.   Oleic acid.   Oleophosphoric acid.

This formula would give a plausible explanation of the decomposition-products observed by Frémy, as well as of those observed by

a. Formation of olein and phosphoric acid:

$$PO^5,HO,2C^{78}H^{71}O^9 + 4HO = PO^5,3HO + 2C^{78}H^{72}O^{10}.$$

Oleophosphoric acid.   Diolein.
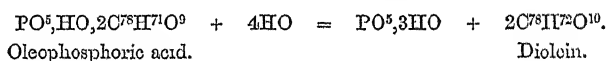
b. Formation of phosphoglyceric acid and oleic (or margaric acid):

$$PO^5,HO,2C^{78}H^{71}O^9 + 10HO = PO^5,2HO,C^6H^7O^5 + 4C^{36}H^{34}O^4 + C^6H^8O^6.$$

Oleophosphoric acid.   Phosphoglyceric acid.   Oleic acid.   Glycerin.

Greater probability, however, appears to belong to Gobley's view which supposes that the olein yielded by the decomposition of Frémy's oleophosphoric acid was contained in it beforehand (Kr.).

d. Fat of Blood. — Human blood contains, according to Lecanu, a solid unsaponifiable, and a liquid saponifiable fat. According to Boudet, it contains cholesterin, serolin, brain-fat (cerebrin?), and a soapy compound. The fat of venous blood is similar in comparison to that of yolk of egg, bile, &c. (p. 484), consisting of olein, margarin, cholesterin, cerebrin and lecithin (p. 484), which substances are extracted by ether from the recently discharged blood. Fatty acids are not present in fresh blood, either in the free state or as salts, but are produced from the lecithin when putrefaction commences. Boudet's serolin is a mixture of olein, margarin, cholesterin, and adhering albumin (Gobley). See Verdeil & Marcet, below.

When freshly discharged blood is mixed with a very large excess of alcohol, the precipitated flocks further exhausted with boiling alcohol, the solutions evaporated, and the residue taken up with ether, the resulting ethereal solution leaves on evaporation a red-brown mixture of solid and liquid fat, which latter dissolves alone on treating the mixture with alcohol. — The *solid fat*, after recrystallisation from boiling alcohol, forms white, pearly, inodorous, tasteless, neutral scales, which are unsaponifiable, melt at 150°, and at a higher temperature give off ammoniacal products and leaves a residue containing phosphoric acid. It is insoluble in cold, easily soluble in boiling alcohol, and separates from the hot concentrated solution, as an oil, from the dilute solution in crystals. It is easily soluble in ether. — The *oil* obtained by evaporating the alcoholic solution is yellowish-brown, of the consistence of turpentine, has a sharp taste, faint odour, and when heated, gives off ammoniacal vapours, and leaves a residue containing phosphoric acid. It is saponifiable and dissolves in alcohol and in ether (Lecanu, *Ann. Pharm.* 48, 308).

When dried blood-serum, previously freed by hot water from the

greater part of the salts contained in it, is treated with boiling alcohol, the alcoholic solutions on cooling deposit Boudet's serolin, and on further evaporation, there remains a yellowish-brown residue which dissolves in alcohol, leaving a quantity of brain-fat. The alcoholic solution deposits cholesterin, and when further evaporated, leaves a glutinous residue still containing brain-fat. On extracting this substance, dissolving the residue in ether, which leaves salts undissolved, and evaporating the ethereal solution, there remains a soft translucent *soap*, which dissolves in alcohol, ether, and water—the aqueous solution being frothy and alkaline—and when mixed with acids, yields oleic acid, margaric acid, and brain-fat (Boudet). This soap agrees therefore with Gobley's viscous matter. — *Serolin* forms microscopic threads and spherules, melting at 36°, not altered by potash-ley, hydrochloric acid, or acetic acid. When subjected to dry distillation, it gives off alkaline vapours, partly distils over without apparent alteration, and leaves a small quantity of charcoal. It is insoluble in cold water, floats as an oil upon hot water, is nearly insoluble in hot alcohol of 36°, but dissolves easily in ether (Boudet, *Ann. Chim. Phys.* 52, 337).

When fresh ox-blood, freed from fibrin by whipping, is mixed with half its weight of water, heated in the water-bath till the albumin coagulates, strained through linen, then mixed with pulverised gypsum, and evaporated over the water-bath to one-fourth, fatty acids [stearic, margaric, and oleic (Marcet, *Arch. Ph. nat.* 18, 151; *Lieb. Kopp's Jahresber.* 1851, 587)] separate out, together with other substances. The filtrate, from which ether takes up cholesterin and serolin (Marcet), deposits chloride of sodium on further concentration, and if boiled with alcohol, after the removal of this salt, yields serolin to the alcohol; and on concentrating and cooling the alcoholic solution, and then adding a little water, the serolin is deposited in white pearly crystals insoluble in water (Verdeil & Marcet, *N. J. Pharm.* 20, 89; abstr. *Lieb. Kopp's Jahresber.* 1841, 586).

If blood, as it issues from the vein, be received in ether, the liquid shaken, the ethereal layer which rises to the surface on standing, replaced by fresh ether, and this treatment repeated a great number of times, the separation of an ethereal layer ceases at last. The liquid is then filtered; the fibrin remaining on the filter, as well as the dark red liquid which runs through, is treated with ether; the several ethereal extracts are united, and the ether is distilled off. There then remains a yellowish fat, whence boiling alcohol extracts lecithin, cerebrin, and cholesterin, leaving olein and margarin free from phosphorus undissolved (Gobley, *N. J. Pharm.* 21, 241).

c. Phosphoretted oil of Peas. — This oil is obtained from the sweet pea with black embryo, by exhausting with ether, evaporating the solution, redissolving in ether, evaporating, and drying at 80°. — It is brown-red, golden-yellow in thin layers, still viscid at 80°, nearly inodorous in the cold, but smells sweetish at 80°. Contains, on the average, 66·87 p. c. C., 9·53 H., 22·35 O., and 1·25 phosphorus, no nitrogen or sulphur. Knop regards it as a solution of an organic phosphoretted compound in fat. — Easily turns rancid. Takes fire when heated on platinum-foil, leaving a difficultly combustible cinder containing phosphoric acid. Does not give up any phosphoric acid to water. Difficult to saponify. — Insoluble in water and in alcohol of 80 p. c., but dissolves in all proportions in ether (W. Knop, *Pharm. Centr.* 1854, 759`
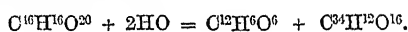
FIRST APPENDIX TO COMPOUNDS CONTAINING 34 AT. CARBON.

A. *Quercetic Acid and Conjugated Compounds.*

Quercetic Acid.

$$C^{34}H^{12}O^{16} = C^{34}H^{12}O^{10},O^{6}.$$

HLASIWETZ.   *Ann. Pharm.* 112, 96.

Formation. Quercetin is resolved by boiling with potash-ley, into quercetic acid and phloroglucin :

$$C^{16}H^{16}O^{20} + 2HO = C^{12}H^{6}O^{6} + C^{34}H^{12}O^{16}.$$

Preparation. A hot very concentrated solution of 3 pts. potash-hydrate is boiled down in a silver basin with 1 pt. quercetin, and the residue is heated, till a sample dissolved in water on a watch-glass no longer gives a flocculent precipitate with hydrochloric acid, and the residue quickly turns dark-red at the edges ; it is then immediately diluted with water and neutralised with hydrochloric acid. After being left to cool and stand for a while, it is filtered from the separated flocks, which contain quercetin and alpha-quercetin ; the filtrate is evaporated to dryness ; the residue exhausted with alcohol ; the alcohol distilled off from the brown tincture ; and the residue diluted with water. On adding neutral acetate of lead to this solution, quercetate of lead is precipitated (phloroglucin remaining in solution), which may be decomposed under water by hydrosulphuric acid. After the sulphide of lead has been filtered off and washed with boiling water, the solutions are evaporated in a current of hydrogen, and the crystals which separate after some days, are collected and decolorised by recrystallisation, with addition of animal charcoal.

Properties. The crystals of quercetic acid are converted by prolonged drying at 120°—130°, into anhydrous quercetic acid. The anhydrous compound partly sublimes in the test-tube. Its aqueous solution has a slight acid reaction. Taste astringent.

	Between 120° and 130°.			Hlasiwetz. *mean.*
34 C	204		59·30	59·44
12 H	12		3·48	3·73
16 O	128		37·22	36·83
$C^{34}H^{12}O^{16}$	344		100·00	100·00

Zwenger & Dronke suggest the formula $C^{12}H^{14}O^{20}$, which requires 59·15 p. c. C. and 3·28 H., basing it upon their formula for quercetin (p. 490). — Perhaps homologous with ellagic acid (p. 183). Related to æsculetin (p. 23) in the same manner as acetic to acrylic acid (Hlasiwetz).

Decompositions. 1. The aqueous solution turns yellow on exposure to the air. — 2. A very dilute *alkaline* solution exposed to the air, acquires first a yellow, then a splendid carmine-red colour. 1 milligrm. quercetic acid imparts a distinct and beautiful rose-red tint to 10 litres

of water. — 3. Quercetic acid heated with oil of vitriol dissolves with red-brown colour, and is precipitated by water in red flocks which form purple solutions with ammonia and with potash-ley (Hlasiwetz). — 4. When boiled with *chloride of acetyl* in an open vessel, it is scarcely altered, but when heated therewith to 100° in a sealed tube, it is quickly converted into biaceto-quercetic acid. At the same time a second product is formed, which colours ferric hydrochlorate deep green, remains in solution after the biaceto-quercetic acid has crystallised out, is precipitated by water in white flocks containing 59·08 p. c. C., 3·91 H., and is perhaps aceto-quercetic acid $C^{34}H^{11}O^{16}, C^4H^3O^2$? (Pfaundler).

Combinations. With *Water*. — A. *Crystallised Quercetic acid*. Slender, silky needles, which effloresce in a warm atmosphere, give off, on the average, 15·49 p. c. water between 120° and 130°, and therefore consist of $C^{34}H^{12}O^{16} + 7$ aq. (calc. = 15·47 p. c. water).

B. *Aqueous Quercetic acid*. — Quercetic acid dissolves sparingly in cold, easily in boiling water, and quickly crystallises therefrom.

Quercetic acid is coloured black-blue by sesquichloride of iron, or, in very dilute solution, a splendid bright blue (Hlasiwetz). When dissolved in water simultaneously with *urea*, it forms a compound, and with excess of urea, gradually a product of decomposition (Pfaundler).

Quercetic acid is soluble in *alcohol* and in *ether*.

Conjugated Compounds of Quercetic Acid.

a. With Acetyl.

Biaceto-quercetic Acid.

$$C^{42}H^{16}O^{20} = C^{24}H^{10}O^{16}, 2C^4H^3O^2.$$
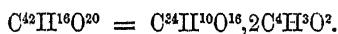
L. Pfaundler. *Wien. Akad. Ber.* 43, 485; *Ann. Pharm.* 119, 213; *Zeitschr. Chem. Pharm.* 4, 521; *Rép. Chim. pure* 3, 452.

Quercetic acid is heated with chloride of acetyl in a sealed tube immersed in a water-bath; the excess of chloride of acetyl is expelled after the action is over; and the glutinous varnish which remains is drenched with water, whereupon it yields resinous flocks, which may be purified by washing with water and recrystallisation from alcohol.

		Small needles.		Pfaundler.
42 C	252	58·87	58·86
16 H	16	3·73	4·01
20 O	160	37·40	37·13
$C^{34}H^{10}O^{16}, 2C^4H^3O^2$	428	100·00	100·00

Biaceto-quercetic acid is decomposed by *heat*, with formation of acetic acid. It dissolves in *oil of vitriol* with yellow colour; in *alkalis* also with yellow colour, changing to red on exposure to the air. — It reduces alkaline solutions of *copper* and *silver-salts*. — Scarcely colours an alcoholic solution of *ferric chloride*.

Insoluble in *water*, whether cold or boiling, easily soluble in *alcohol*.

b. With Phloroglucin (xv, 65).

1. Quercetin.

$$C^{46}H^{16}O^{20} = C^{34}H^{10}O^{14}, C^{12}H^6O^6 ?$$

RIGAUD.   *Ann. Pharm.* 90, 283.
HLASIWETZ.   *Ann. Pharm.* 112, 96.
ZWENGER & DRONKE.   *Ann. Pharm. Suppl.* 1, 261. — *Ann. Pharm.*
    123, 153.

Discovered by Rigaud in 1854. — Called *Meletin* by Stein.

Occurrence.   Quercetin exists ready formed in Persian berries (p. 72).
These berries drenched with ether yield a gold-yellow solution, from
which, by evaporating the ether, precipitating with water, redissolving
in alcohol, and evaporating slowly with addition of water, a yellow,
finely divided deposit is obtained, consisting of microscopic, transpa-
rent, silky, crystalline needles.   These contain 58·87 p. c. C., 4·66 H.,
— after drying at about 100°, 60·24 C., 4·18 H., and therefore consist
of quercetin, with which they likewise agree in their reaction with
neutral acetate of lead and nitrate of silver (Bolley, *Ann. Pharm.*
115, 54).
It exists in conjugated combination with sugar, in quercitrin, rutin,
and robinin.
The following substances yield quercetin by their decomposition ;
but it is doubtful whether they are identical with the glucosides
mentioned :—
a. A yellow colouring matter from ripe horse-chestnuts, likewise
found in the full-grown, but not in the undeveloped leaves, not in the
bark, and in extremely small quantity only in the yellow leaves.   From
the flowers of the horse-chestnut, Rochleder obtained quercitrin and
quercetin ; from the leaves, quercæscitrin (p. 500).   Rochleder (*Wien.
Akad. Ber.* 33, 565. — *J. pr. Chem.* 87, 35. — *Ann. Pharm.* 112, 112.
b. Hops contain a yellow dye which behaves to reagents like
quercitrin, and like that compound is also resolvable into quercetin and
sugar (R. Wagner, *Dingl.* 154, 65 ; *Chem. Centr.* 1859, 892).
c. The berries of the Sea Buckthorn or Sallowthorn (*Hippophae
rhamnoïdes*) after being pressed, boiled with water, and again dried,
yield to boiling alcohol a colouring matter, which is precipitated from
this solution by basic acetate of lead, remains mixed with the sulphide
of lead when the washed precipitate is decomposed under water by
hydrosulphuric acid, and may be extracted therefrom by hot alcohol.
On evaporating the alcoholic solution, and freeing the residue from
traces of fat by ether, quercetin remains, and may be purified by solu-
tion in alcohol and crystallisation, or by precipitation with water.
After drying between 100° and 110°, it contains, on the average, 60·73
p. c. carbon, and 3·60 hydrogen, forms in alcoholic solution a nearly
orange-coloured precipitate with neutral acetate of lead, and exhibits
the other reactions of quercetin (Bolley, *Dingl.* 162, 143 ; *Kopp's
Jahresber.* 1861, 708).
d. A loose brown-yellow powder imported from North America,
under the name of *Flavin* (perhaps prepared from quercitron-bark by

boiling with carbonate of soda, supersaturating and boiling for some time with sulphuric acid), yields to ether, quercetin (containing 58·70 p. c. C., 4·08 .H), but likewise contains foreign substances and products of decomposition, which impede its preparation in the pure state. (Bolley & Brunner, *Schweiz. polyt. Zeitschr.* 2, 51 and 92). Flavin imported in 1853 contained quercitrin, which could be obtained from it by boiling with very dilute sulphuric acid, and recrystallising the flocks which separated on cooling. It contained at 100°, 53·46 p. c. C., 4·96 H., and 41·58 O. (König, *J. pr. Chem.* 71, 98).

e. The green leaves of plants contain either quercitrin or quercetin ; also the flowers (Filhol, *N. J. Pharm.* 41, 151 ; *Pharm. Viertelj.* 12, 232). — The flowers of *Cornus mascula*, and the skin of *Agaricus ochreaceus* contain quercetin, robinin or rutin ; the latter appears also to be contained in the flowers of *Leucojum vernum*, and *Acer Pseudoplatanus* (Stein).

Rhamnetin (p. 75) and thujetin (p. 244) are regarded by Hlasiwetz as possibly identical with quercetin, which however is doubted by Bolley in the case of rhamnetin.

Formation and Preparation. Quercetin is produced by boiling quercitrin (Rigaud), rutin (Rochleder & Hlasiwetz) and robinin (Zwenger & Dronke) with aqueous mineral acids,—in all cases together with sugar or a similar body, and separates, partly during the boiling and on cooling, partly only after the liquid has been left at rest for some time. — It is likewise obtained in the preparation of quercitrin by the method presently to be described (p. 496).

Crystallised quercetin may be freed from its water, amounting to between 6·9 and 10·4 p. c. by drying between 100° and 120° (Zwenger & Dronke) during which, so far as appears from the descriptions, it suffers no external alteration, beyond sometimes acquiring a greenish colour.

Properties. Small, very slender, bright-yellow needles, which do not polarise light (according to Stein they polarise strongly), or a lemon-yellow powder (Rigaud. Zwenger & Dronke). Melts above 251° to a yellow liquid, without decomposition when quickly heated (see below), and then solidifies in the crystalline form on cooling (Zwenger & Dronke). At a higher temperature, it sublimes, partly undecomposed, in yellow needles (Hlasiwetz. Zwenger & Dronke). Tasteless (Rigaud, Stein): in aqueous solution it has a slightly saline, somewhat astringent taste (Zwenger & Dronke), strongly bitter like that of quinine (Stein). Inodorous, permanent in the air, neutral.

Calculations.

According to Wurtz *and* Zwenger & Dronke.

26 C	156	......	59·54
10 H	10	....	3·81
12 O	96	....	36·65
$C^{26}H^{10}O^{12}$	262	....	100·00

According to Hlasiwetz.

a.

92 C	552	.....	60·46
33 H	33	....	3·61
41 O	328	....	35·93
$2C^{46}H^{16}O^{20},HO$	913	....	100·00

According to Hlasiwetz.

	b.			*c.*	
46 C	276	59·87	46 C	276	58·72
17 H	17	3·66	18 H	18	3·83
21 O	168	36·47	22 O	176	37·45

$C^{46}H^{16}O^{20},HO$... 261	100·00	$C^{46}H^{16}O^{20},2HO$.. 470	100·00

Analyses in mean numbers.

	Rigaud.	Hlasiwetz.		Schützenb. & Paraf.
		at 220°.	*at 200°.*	*at 150°.*
C	59·23	59·73	60·31	59·61
H	4·11	3·73	3·62	3·41
O	36·66	36·54	36·07	36·98
	100·00	100·00	100·00	100·00

	Zwenger & Dronke.			Stein.	
	a. *at 100°.*	*b.* *at 120°.*	*c.* *at 120°.*	*at 100°* to	*105°.*
C	59·20	59·89	59·64	59·06 to	60·39
H	4·48	3·62	3·72	3·76	4·23
O	36·32	36·49	36·64	. 37·18	35·38
	100·00	100·00	100·00	100·00	100·00

a prepared from robinin, *b* from quercitrin, *c* from rutin (Zwenger & Dronke) ; the samples of quercetin analysed by Rigaud and by Hlasiwetz were also prepared from quercitrin ; those analysed by Stein, from rutin.— Quercetin which has been dried for some time at 120°, is, according to Zwenger & Dronke, already somewhat altered, and has acquired a greenish tinge ; according to Hlasiwetz, however, the water of crystallisation is not completely expelled at (100° or) 120°, perhaps not even between 200° and 220° : hence, in the formulæ *a* and *b*, corresponding to quercetin dried at these temperatures, Hlasiwetz supposes water of crystallisation to be still present. Quercetin heated with alcoholic hydrochloric acid, separated when the alcohol was distilled off, in deep orange-yellow crystals, containing, after drying in the air, 58·3 p. c. carbon and 3·7 hydrogen. For these crystals Hlasiwetz assumes the formula *c*.
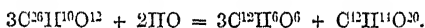
Besides the above, the formulæ $C^{24}H^9O^{11}$ (Rigaud) and $C^{20}H^7O^9$ (Stein) have been proposed for quercetin. The formula proposed by Wurtz (*N. Ann. Chim. Phys.* 42, 244) and adopted by Zwenger & Dronke, agrees well with the quantities of quercetin and sugar obtained from robinin, rutin, and (by Rigaud) from quercitrin, but does not explain so well as that of Hlasiwetz the formation of quercetic acid from quercetin. Moreover, no attempt has yet been made to deduce from this formula the composition of alpha-quercetin or of the different quercitrins of Rigaud, Hlasiwetz and Rochleder.

Decompositions. 1. When quercetin is slowly heated above 200° it changes colour, and is converted, between 230° and 250°, into an interlaced mass, consisting of large shining needles of sublimed quercetin mixed with a dirty-coloured powder ; a large portion is at the same time decomposed, with separation of charcoal (Hlasiwetz, Zwenger & Dronke). According to Stein, it gives off at 200°, water containing formic acid, and then dissolves with brown colour in boiling absolute alcohol, leaving, however, a brown residue.— 2. Warm concentrated *hydrochloric acid* colours quercetin orange- to brown-yellow (Rigaud). From solution in alcoholic hydrochloric acid, quercetin separates, on concentration, in deep orange-yellow crystals, which retain their colour when recrystallised from alcohol, and from whose solution water throws down straw-yellow quercetin. (See the analysis above given of the dark-coloured crystals). No phloroglucin is produced even by boiling quercetin for a day with

moderately concentrated hydrochloric acid, and when a solution of quercetin in acetic acid, saturated with hydrochloric acid gas, is heated to 120°, only a trace of it is decomposed, the rest merely acquiring a darker colour (Hlasiwetz). Quercetin is but little altered by twelve hours' boiling with moderately dilute sulphuric acid; but on heating it for twelve hours with alcohol and hydrochloric acid, a brown mixture of undecomposed quercetin and amorphous granules is obtained (the latter consisting of Stein's *Mellulmin*), containing from 62·43 to 63·17 p. c. carbon, and 5·07 to 5·18 hydrogen. Formic acid and a small quantity of carbonic acid are produced at the same time (Stein). — 3. Cold *nitric acid* attacks quercetin easily, colouring it first greenish, then brown-red, and dissolving it with reddish colour; on heating the liquid, nitrous acid is violently evolved and oxalic acid formed, together with a small quantity of picric acid (Zwenger & Dronke). — 4. Quercetin very easily reduces *nitrate of silver* at ordinary temperatures; in warm moderately dilute solutions, it generally produces a transient blood-red colour (Bolley, Zwenger & Dronke). It reduces *cupric oxide* in alkaline solution (Stein), and *terchloride of gold* quickly at the boiling heat (Zwenger & Dronke). — 5. When heated, or left for some time in contact with aqueous ammonia, it forms quercetamide (Schützenberger & Paraf). — 6. By boiling with very strong *potash-ley*, it is converted into quercetic acid (p. 488) and phloroglucin (xv. 63):

$$C^{16}H^{16}O^{20} + 2HO = C^{34}H^{12}O^{16} + C^{12}H^6O^6 \text{ (Hlasiwetz).}$$

Formation of quercetic acid, according to Zwenger & Dronke:

$$3C^{26}H^{10}O^{12} + 2HO = 3C^{12}H^6O^6 + C^{12}H^{14}O^{30}.$$
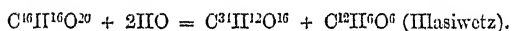
Alpha-quercetin (p. 494) may also be formed at the same time. Baryta-water does not effect the decomposition. On heating quercetin with potash-ley, in a sealed tube, to 160°, no further decomposition takes place (Hlasiwetz). — 6. Quercetin dissolved in water or in alcohol, forms, when treated with *sodium-amalgam*, a product of a fine red colour, changed to green by alkalis and neutral acetate of lead, and red again by acids; it contains 55·21 p. c. carbon, 5·87 hydrogen, and 38·92 oxygen: Stein's *Paracarthamin* (Stein). The alkaline solution of quercetin, treated with sodium-amalgam, easily and quickly yields the whole of the phloroglucin contained in it, together with a second colourless product different from quercetic acid (Hlasiwetz, *Ann. Pharm.* 124, 358; *Chem. Centr.* 1863, 272). — 8. With *ferric hydrochlorate* it assumes a dark-green colour (Rigaud), even in very dilute solutions, and becomes dark-red when heated (Zwenger & Dronke). When an alcoholic solution of quercetin is mixed with an alcoholic solution of ferric chloride and evaporated, there remains a black-green, non-crystalline mass, from which water dissolves traces, acquiring a green colour, which disappears on boiling. Alcohol and ether dissolve the mass completely, forming solutions having the colour of chlorophyll. Oil of vitriol dissolves it with green colour changing to yellow, and water added to the solution throws down yellow flocks. Hot glacial acetic acid dissolves only traces of the green mass; the solution in hydrochloric acid is green at first, but afterwards becomes yellow (Pfaundler, *Ann. Pharm.* 115, 44).

Combinations. With Water. A. *Crystallised Quercetin.* See above.

B. *Aqueous solution.* — Quercetin is nearly insoluble in cold water, and but slightly soluble in boiling water, with yellowish colour.

With Hydrochloric acid.

Quercetin dissolves easily in *alkaline* liquids, forming golden-yellow solutions, from which it is precipitated by acids in flocks. The ammoniacal solution deepens in colour when exposed to the air (Rigaud, Zwenger & Dronke).

Alcoholic quercetin precipitates *neutral acetate of lead* brick-red (Bolley); the precipitate decomposes when washed with alcohol (Zwenger & Dronke).

Protochloride of iron scarcely affects the aqueous solution, but colours the alcoholic solution dark-red (Zwenger and Dronke). — With *sesquichloride of iron*, see above.

Quercetin dissolves in warm *acetic acid*, and is precipitated almost entirely on cooling (Rigaud). — It dissolves readily in *alcohol*, even when very dilute, much less freely in *ether* (Rigaud. Zwenger & Dronke). It dissolves in 18·2 parts of boiling, and in 229·2 parts of cold absolute alcohol (Stein). Quercetin dyes linen a pure and bright yellow (Rigaud).

2. Alphaquercetin.

$$C^{58}H^{20}O^{24} = C^{34}H^{10}O^{14},2C^{12}H^{5}O^{5} ?$$

HLASIWETZ.   *Ann. Pharm.* 112, 102.

When quercetin is decomposed by caustic potash for the preparation of quercetic acid, the fused mass dissolved in water, and the solution neutralised with hydrochloric acid, green-yellow flocks separate out, which, after washing, dissolve in a large quantity of boiling water, leaving quercetin undissolved. The filtrate, on standing and concentrating, deposits alphaquercetin in light, shining, greenish-yellow scales.

	at 100°.			Hlasiwetz. mean.
58 C	348	... ...	62·14	62·32
20 H	20	... ...	3·57	4·17
24 O	192	... ...	34·29	33·51
$C^{58}H^{20}O^{24}$	560	... ...	100·00	100·00

Perhaps identical with lutoolin (xv, 28) (Hlasiwetz).

Alphaquercetin is decomposed by *caustic potash* in the same manner as ordinary quercetin, but more slowly. The decomposition may probably be expressed thus:

$$C^{58}H^{20}O^{24} + 4HO = C^{34}H^{12}O^{16} + 2C^{12}H^{4}O^{6}.$$
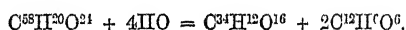
When exposed to the air in alkaline solution, it assumes a fine green colour, not brown like ordinary quercetin. — It reduces aqueous *silver*-

Alphaquercetin is scarcely soluble in cold, but completely soluble in boiling *water*. — Its alcoholic solution colours *sesquichloride of iron* dirty dark-green. — It is thrown down from its solutions by *charcoal*.

Quercetamide.

Schutzenberger & Paraf. *Mulhous. Soc. Bull.* 1861, 507 ; *Zeitschr. Chem. Pharm.* 5, 41.

Formation and Preparation. When quercetin is dissolved in aqueous ammonia and allowed to stand for some months in a closed vessel, it is partially converted into quercetamide. The same conversion takes place more quickly and completely when the solution is heated to 145° or 150°, for 12 hours, in a sealed tube, the solution becoming brown, and depositing a large quantity of quercetamide. The contents of the tube are poured into a vessel filled with carbonic acid, and the excess of ammonia is expelled by heating the liquid and passing through it a stream of carbonic acid ; the residue is dissolved in hydrochloric acid, filtered from an undissolved decomposition-product of quercetamide, and neutralised with ammonia. The brown precipitate thus formed is washed with boiling water by decantation, with the least possible exposure to the air, and afterwards dried in a vacuum. It is not possible to prevent altogether the admixture of a substance produced by the action of the air.

Properties. Amorphous, dark-brown mass. Contains, at 130°, 52·05 p. c. C, 4·36 H; or 51·61 p. c. C, 4·70 H, and 9·71 N. According to Schützenberger & Paraf, it is produced by the combination of quercetin and ammonia, without elimination of water, and is therefore either $C^{24}H^9O^{11}, 2NH^3$ or $C^{26}H^{10}O^{12}, 2NH^3$ or $C^{16}H^{16}O^{20}, 4NH^3$, according to the formula assigned to quercetin. The proportion of hydrogen found by analysis is less than is required by either of these formulæ, probably on account of some change having occurred in the quercetamide.

Decompositions. Quercetamide melts when heated on platinum-foil, and leaves a large quantity of charcoal when burnt. — It blackens very quickly on exposure to the air, especially in ammoniacal solution, and is converted in a few hours into a substance which is insoluble in hydrochloric acid, alkalis, or alcohol, and contains 47·69 p. c. C, 2·91 H, 10·23 N, and 39·14 O.

Quercetamide dissolves slightly in *water.* It is soluble in hydrochloric acid, and is precipitated from the solution by ammonia; an excess of *ammonia* re-dissolves the precipitate. The solution in hydrochloric acid is slightly changeable. — Dissolves in *alcohol* and *ether.*

c. With Phloroglucin and Sugar (Glucosides of Quercetin).

1. Quercitrin.

Chevreul. *J. Chim. méd.* 6, 157.
Brandt. *N. Br. Arch.* 21, 25.
Bolley. *Ann. Pharm.* 37, 101. — *Ann. Pharm.* 62, 136.

RIGAUD. *Ann. Pharm.* 90, 283; abstr. *Pharm. Centr.* 1854, 729; *J. pr. Chem.* 63, 94; *N. Ann. Chim. Phys.* 42, 244; *Chem. Gaz.* 1854, 428; *Lieb. Kopp's Jahresb.* 1854, 615; Preliminary notices: *Ann. Pharm.* 88, 136; *J. pr. Chem.* 61, 448.

HLASIWETZ. *Wien. Akad. Ber.* 17, 375; *Ann. Pharm.* 96, 123; *J. pr. Chem.* 67, 97; *Chem. Centr.* 1856, 57; *Lieb. Kopp's Jahresber.* 1855, 698. — *Wien. Akad. Ber.* 36, 401; *Ann. Pharm.* 112, 96; *J. pr. Chem.* 78, 257; abstr. *Chem. Centr.* 1860, 132; *Rép. Chim. pure,* 2, 139; *Lieb. Kopp's Jahresb.* 1859, 524.

ROCHLEDER. *Wien. Akad. Ber.* 33, 565; *J. pr. Chem.* 77, 31; *Chem. Centr.* 1859, 166; *Lieb. Kopp's Jahresb.* 1859, 522.

STEIN. *Dresdener. polyt. Schulprogr. April,* 1862; *J. pr. Chem.* 85, 351; *Chem. Centr.* 1862, 359; *Rép. Chim. pure,* 5, 108. — *J. pr Chem.* 88, 280; *Zeitschr. Chem. Pharm.* 6, 260.

ZWENGER & DRONKE. *Ann. Pharm. Suppl.* 1, 266; *Lieb. Kopp's Jahresb.* 1861, 762.

Quercitric acid (Bolley). *Quercimelin* (Stein). — First investigated by Bolley. — Occurs in the bark of *Quercus tinctoria.* Formerly regarded as identical with rutin (p. 500), which view was refuted by Stein and Zwenger & Dronke. Preisser's erroneous statements respecting quercitrin were disproved by Bolley.

Even setting aside rutin, robinin, queræscitrin, and the substances mentioned below, the identity of which with quercitrin is doubtful, the bodies described as quercitrin still exhibit certain differences, the substance investigated by Hlasiwetz yielding, when decomposed by acids, 1 at. sugar to each at. quercetin ($C^{46}H^{16}O^{20}$), while that investigated by Rigaud yielded 2 at. sugar. The queræscitrin of Rochleder, which gave 3 at. sugar to 1 at. quercetin, may be regarded as forming the third member of this series. The distinction between Rigaud's and Hlasiwetz's quercitrin hereby indicated cannot, however, for the present, be carried out, inasmuch as it remains doubtful, in many ways, to which of the two the other statements refer. Hlasiwetz (*epist. comm*) further obtained from quercitron-bark a body resembling quercetin, but yielding, by decomposition, not quercetin-sugar, but isoldulcite, $C^{12}H^{14}O^{12}$, in large crystals like sugar-candy; this result indicates the existence in quercitron bark of a quercetin-compound bearing the same relation to quercitrin as the latter bears to rutin and robinin.

According to Stein, morindin (p. 190) may be identical with quercitrin, and according to Hlasiwetz also rhamnin (p. 80) and thujin (p. 245), which is doubted by Bolley.

Preparation. From the Quercitron-bark of commerce. 1. The bark is boiled with water, the decoction is left to cool, and the impure quercitrin which separates is collected. It is then rubbed to a pulp with alcohol of 35° B., heated over the water-bath, and collected on linen and pressed, whereby the principal impurities are removed. The residue is dissolved in a larger quantity of boiling alcohol, the solution is filtered hot, and water is added to it till it becomes turbid, so that the greater part of the quercitrin separates before the liquid is quite cold. It is collected, pressed, and purified by a repetition of the same treatment (Rochleder). The quercitrin remaining in the bark is obtained as quercetin by decomposing a second decoction with hydrochloric acid in the cold, then filtering and heating to the boiling point, the quercetin then separating. It is to be filtered whilst hot, as afterwards only a little impure quercetin is deposited from the solution (Rochleder). — 2. The pulverised bark is exhausted with six parts of alcohol of sp. gr. 0·84 in a percolator till the liquid is of a bright wine colour. The tincture is freed from tannic acid by precipitation with washed ox-bladder or isinglass-solution, and filtered; and after adding water, the alcohol is distilled off, when a quantity of brown resinous drops first separates, and afterwards quercitrin crystallises out. The

crystals are collected before remaining too long in the mother-liquor, then washed with cold water, and dissolved in absolute alcohol, and the filtrate, after addition of water, is evaporated till it crystallises (Bolley, Rigaud). — 3. The bark, in small pieces, is exhausted with boiling alcohol; the alcohol is distilled off; and the residue, while still warm, is mixed with a little acetic acid, and then with neutral acetate of lead; the filtrate, freed from lead by hydrosulphuric acid, is evaporated; and the quercitrin which crystallises is purified by repeated crystallisation from alcohol (Zwenger & Dronke). — Stein apprehends, in this process, a decomposition of the quercitrin by the free acetic acid.

Properties. Hydrated quercitrin forms microscopic, partly rectangular, partly rhombic tables, having their two obtuse lateral edges truncated, and varying in colour from sulphur- to chrome-yellow (Bolley, Rigaud). The tables are thicker, harder, and of a deeper yellow than those of rutin (Stein). Pale lemon-yellow when powdered (Bolley). According to Stein, the crystals exhibit splendid colours in polarised light; according to Rigaud they do not. Neutral (Zwenger and Dronke). Inodorous, tasteless; in solution it tastes faintly bitter (Zwenger and Dronke); in a solution prepared with hot water, distinctly bitter; in alcoholic solution, more strongly than rutin (Stein). Permanent in the air. — After dehydration, it melts at 160° to a dark-yellow resin, which solidifies to an amorphous mass on cooling (Zwenger and Dronke).

Air-dried quercitrin, $C^{38}H^{18}O^{20} + 6$ aq., loses at 100°, on an average, 5·74 p. c. water (3 at. $= 5·86$ p. c. HO), and when heated to 165° for some time, a further quantity, amounting altogether to 11·81 p. c. ($= 6$ at.) of the air-dried quercitrin (by calc. 11·78 p. c. HO) (Zwenger & Dronke). According to Illasiwetz, on the other hand, the formula of anhydrous quercitrin, containing 1 at. sugar to each at. quercetin, is $C^{58}H^{30}O^{34}$, and of that containing 2 at. sugar $C^{70}H^{30}O^{40}$, hydrated quercetin being $C^{58}H^{30}O^{34} + HO$, or $C^{70}H^{36}O^{40} + 2HO$.

Calculations.
According to Zwenger & Dronke.

I. Hydrated.				II. Anhydrous.			
38 C		228	52·65	38 C		228	56·15
21 H		21	4·84	18 H		18	4·43
23 O		184	42·51	20 O		20	39·42
$C^{38}H^{21}O^{20} + 3Aq.$		433	100·00	$C^{38}H^{18}O^{20}$		266	100·00

According to Illasiwetz.

III. Hydrated.				IV. Anhydrous.			
58 C		348	52·8	58 C		348	53·53
31 H		31	4·7	30 H		30	4·61
35 O		280	42·5	34 O		242	41·86
$C^{58}H^{30}O^{34} + Aq.$		659	100·0	$C^{58}H^{30}O^{34}$		620	100·00

According to Illasiwetz.

V. Hydrated.				VI. Anhydrous.			
70 C		420	52·89	70 C		420	54·12
38 H		38	4·79	36 H		36	4·64
42 O		256	42·32	40 O		320	41·24
$C^{70}H^{36}O^{40} + 2Aq.$		714	100·00	$C^{70}H^{36}O^{40}$		776	100·00

Analyses in mean numbers.

	a. Bolley. at 100°.	b. Hlasiwetz. at 100°.	c. Zwenger & Dronke. at 100°.
C	52·18	52·50	52·39
H	4·95	5·04	4·91
O	42·57	42·46	42·70
	100·00	100·00	100·00

	d. Rigaud.	e. Hlasiwetz. near the melting-point.	f. Stein.	g. Zwenger & Dronke. at 165°.
C	53·56	54·05	55·75	56·03
H	5·06	5·15	5·19	4·57
O	41·38	40·80	39·06	39·40
	100·00	100·00	100·00	100·00

Bolley gave for crystallised quercitrin the formula $C^{16}H^9O^{10}$, which Rigaud altered to $C^{36}H^{20}O^{21}$. Gerhardt (*Traité,* 4, 331), who regarded phlorizin and quercitrin as homologues, adopted for Bolley's quercitrin the formula $C^{36}H^{18}O^{20}$ + 2HO ; Rigaud's contained 1 at. HO less. Stein, on the contrary, supposes quercitrin to contain equal numbers of atoms of H and O, and adopts the formula $C^{18}H^{10}O^{10}$. See further under rutin (p. 503).
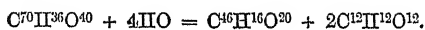
Decompositions. 1. Quercitrin subjected to dry distillation, yields empyreumatic products, together with yellow crystals of quercetin, and leaves a light, difficultly combustible charcoal (Zwenger & Dronke). The sublimed quercetin was formerly thought to be unchanged quercitrin. Crystallised quercitrin became soft on one occasion at 160° to 190°, forming bubbles at last ; on another occasion it became darker at 150° to 180°, softened at 190° to 195°, and melted at about 200°, giving off bubbles and an odour of caramel. The fused mass was transformed by a little boiling water, without dissolving, into amorphous quercetin (Stein). — 2. Solutions of quercitrin acquire a brown-red colour by exposure to the air (Bolley). — Concentrated *nitric acid* produces a violent evolution of nitric oxide and carbonic acid, and forms a clear red-brown solution, which contains oxalic acid (Rigaud). Besides a large quantity of oxalic acid (none according to Stenhouse, *Ann. Pharm.* 98, 179), there is produced a trace of picric acid (Zwenger & Dronke). Dilute nitric acid, when warmed with quercitrin, produces at first the same splitting up as other acids, and afterwards decomposition (Rigaud). — 4. Quercitrin heated with *oxide of manganese* and sulphuric acid (Bolley), with *chromate of potash* and sulphuric acid (Rigaud), yields formic acid. — 5. The dark-brown precipitate produced by *nitrate of silver* in solutions of quercitrin is quickly reduced to the metallic state (Bolley). Quercitrin reduces *nitrate of silver* and *terchloride of gold,* quickly in the cold, *cuprate of potash* only after continued boiling or long standing (Zwenger & Dronke). — 6. *Oil of vitriol* forms with it a solution which soon becomes dark and black (Rigaud).

7. Quercitrin is decomposed by boiling with dilute *mineral acids* into quercetin, which separates, and sugar (Rigaud). The same splitting up is effected by boiling with alum, but not by prolonged heating with acetic acid (Rigaud). See under *Rutin,* the reaction of acetic acid with rutin. Emulsin does not produce decomposition (Zwenger & Dronke). When concentrated hydrochloric acid is used, the quercetin, which is separated, has an orange-red or brown-yellow colour (Rigaud).

100 parts of quercitrin yield, on the average, 44·35 parts of sugar and 61·44 parts of quercetin (Rigaud). Stein obtained 62·9 parts of quercitrin, both it and the quercetin being dried at 110°. These numbers agree approximately with the equation given by Zwenger and Dronke :

$$C^{38}H^{18}O^{20} + 4HO = C^{26}H^{10}O^{12} + C^{12}H^{12}O^{12}.$$
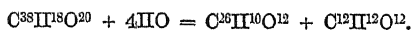
(by calculation 60·50 p. c. quercetin and 41·57 p. c. sugar), also with that of Illasiwetz :

$$C^{70}H^{36}O^{40} + 4HO = C^{46}H^{16}O^{20} + 2C^{12}H^{12}O^{12}.$$

(by calculation 58·06 quercetin, 45·34 sugar). — On the other hand, the quercitrin examined by Illasiwcitz yielded, on an average, 27·87 p. c. sugar, as required by the equation :

$$C^{58}H^{30}O^{34} = C^{46}H^{16}O^{20} + C^{12}H^{12}O^{12} + 2HO.$$
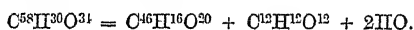
(by calculation 27·4 p. c. sugar).

8. When heated with an insufficient quantity of *baryta-water*, quercitrin partly dissolves to a green-brown liquid, which, on evaporation, leaves a brittle transparent syrup, having an odour of caramel (Bolley).

Combinations. *With Water.* Hydrated quercitrin (see above). — Fused quercitrin takes up water when immersed therein. — Quercitrin dissolves slightly in cold, and in 425 parts of boiling water (Rigaud). It dissolves in 2485 parts of cold, 143·3 parts of boiling water (Stein). The straw-yellow solution is rendered colourless by acids (Zwenger & Dronke).

Quercitrin dissolves very easily in dilute aqueous *ammonia* and in *caustic soda:* the ammoniacal solution deepens in colour by exposure to the air, and ultimately turns dark-brown (Rigaud). Carbonic acid does not precipitate baryta from the neutral solution of quercitrin in *baryta-water* (Bolley).

The *neutral* and *basic acetates of lead* added to solutions of quercitrin throw down the greater part of that substance ; the precipitates dissolve readily in acetic acid (Zwenger & Dronke). One drop of a solution of neutral acetate of lead colours the solution in absolute alcohol deep orange (Stein). A hot alcoholic solution of neutral acetate of lead throws down from alcoholic quercitrin, a splendid yellow precipitate, which contains, after repeated boiling with water and drying at 100°, on an average, 37 p. c. oxide of lead, 33·04 p. c. C., 3·11 H., and 26·85 O. (Bolley).

Aqueous or alcoholic quercitrin is coloured dark-green by *sesquichloride of iron,* even when diluted to 4000 or 5000 times its bulk (Rigaud). Quercitrin is not coloured by *protochloride of iron* at first, but on standing in the air, or when shaken, it turns greenish (Zwenger & Dronke).

Quercitrin dissolves in warm *acetic acid* (Rigaud). It dissolves in 4 or 5 parts of *alcohol,* from which it is precipitated by water ; the solution leaves a thick extract when evaporated, and yields crystals only after addition of water (Rigaud). Soluble in 3·9 parts of boiling, and in 23·3 parts of cold absolute alcohol (Stein). — Dissolves slightly in *ether* (Rigaud).

2. Queræscitrin.

ROCHLEDER.   *Ann. Pharm.* 112, 112.

The leaves of the horse-chestnut yield, instead of quercitrin, fine yellow crystalline grains of the size of poppy-seeds, which split up by the action of hydrochloric acid into quercetin and 56·3 p. c. sugar. They contain, on an average, 52·45 p. c. C., and 5·05 H., corresponding to the formula $C^{82}H^{46}O^{50}$ (calc. = 52·45 p. c. C., and 4·90 H). Their decomposition with hydrochloric acid may be represented thus:

$$C^{82}H^{46}O^{50} + 6HO = C^{16}H^{16}O^{20} + 3C^{12}H^{12}O^{12};$$
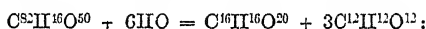
by calculation 75·5 p. c. sugar (Rochleder).

3. Rutin.

WEISS.   *Pharm. Centr.* 1842, 903.
BORNTRAGER.   *Ann. Pharm.* 53, 385.
ROCHLEDER & HLASIWETZ.   *Wien. Akad. Ber.* 7, 817 ; *Ann. Pharm.* 82, 197 ; *J. pr. Chem.* 56, 96 ; abstr. *Pharm. Centr.* 1852, 369 ; *Chem. Gaz.* 1852, 254 ; *Lieb. Kopp's Jahresb.* 1851, 561.
W. STEIN.   *J. pr. Chem.* 58, 399 ; *Pharm. Centr.* 1853, 193 ; *Chem. Gaz.* 1853, 221 ; *Lieb. Kopp's Jahresb.* 1853, 535 ; *Dresdener polyt. Schulprogramm,* April, 1862 ; *J. pr. Chem.* 85, 351 ; *Chem. Centr.* 1862, 369 ; *Rép. Chim. pure* 5, 108 ; *J. pr. Chem.* 88, 280 ; *Zeitschr. Chem. Pharm.* 6, 250.
HLASIWETZ.   *Wien. Akad. Ber.* 17, 375 ; *Ann. Pharm.* 96, 123 ; *J. pr. Chem.* 67, 97 ; *Chem. Centr.* 1856, 57 ; *Lieb. Kopp's Jahresb.* 1855, 698. — *Chem. Centr.* 1862, 419.
ZWENGER & DRONKE.   *Ann. Pharm.* 123, 145 ; *Chem Centr.* 1862, 766.

Rutic acid (Borntrager). *Phytomelin, Melin,* or *Vegetable yellow* (Stein). Formerly held to be identical with quercitrin, the incorrectness of which view was proved by Stein and by Zwenger & Dronke.

Sources. In the common garden rue (*Ruta graveolens*) (Weiss, Bornträger). In capers, the flower-buds of *Capparis spinosa* (Rochleder & Hlasiwetz ; Zwenger & Dronke). In the so-called *Waifa,* the undeveloped flower-buds of *Sophora japonica* (Stein, Th. Martius, *N. Jahrb. Pharm.* 1, 241). See also p. 490.

According to Stein, safflower-yellow (204) is uncrystallisable rutin ; the colouring matter of straw and of *Æthalium, Hippophae,* and *Polygonum Fagopyrum* likewise agree in character with rutin. (See below.)

Preparation. 1. *From Garden rue.* The dried and comminuted plant is boiled for half an hour with common vinegar, and the expressed liquid is set aside for several weeks, or so long as it continues to deposit impure rutin. The deposit is washed with cold water, heated to boiling with 4 parts of acetic acid and 16 parts of water, filtered, and left for some days to crystallise. The crystals obtained thus, and by partial evaporation of the mother-liquor, are dissolved in 6 parts of

boiling water; the solution is treated with animal charcoal; and, after addition of ⅛th of water, the alcohol is distilled off. The rutin crystallises from the residue after some days, the more readily the less strongly the solution is heated (Borntrager, Weiss). A green resin with which the rutin is contaminated is difficult to remove by crystallisation; it is more easily got rid of by acidifying the alcoholic solution with acetic acid, and precipitating with neutral acetate of lead. The filtrate is freed from lead by hydrosulphuric acid, and evaporated, when the rutin crystallises, and may be recrystallised from boiling water. It still contains a substance resembling cumarin, from which it may be freed, though with extreme difficulty, by repeated boiling with ether (Zwenger & Dronke).

2. *From preserved Capers.* —The capers are allowed to stand in water for a few hours, after which the water is poured off, and the capers are pressed; this process is repeated twice to remove salt and vinegar. The decoction obtained by twice boiling the washed capers in not too large a quantity of water, throws down, on standing for 24 hours, a large quantity of yellowish-white flocks, which are collected, dried, and dissolved in boiling alcohol, whereby a jelly-like substance is left undissolved. The alcoholic solution is mixed with water, and the alcohol is distilled off ; the residue then solidifies on cooling, from crystallisation of rutin. The crystals are purified by pressing and recrystallisation from boiling water (Rochleder & Illasiwitz). Zwenger & Dronke add to this solution in hot water a few drops of solution of neutral acetate of lead (too much would precipitate a compound of rutin and lead-oxide), and free the filtrate from lead by means of hydrosulphuric acid.

3. *From Waifa.* The coarsely bruised waifa is repeatedly boiled with alcohol of 80 p. c., and the greater part of the alcohol is distilled off, whereupon the residue thickens to a pulp of impure rutin, amounting to 11 p. c. of the waifa employed. It is crystallised repeatedly from boiling water, and afterwards washed with cold water (Stein). A similar method is adopted by Th. Martius (*N. Br. Arch.* 110, 231). To purify the rutin, hydrated oxide of lead is added to the boiling alcoholic solution, as long as it is coloured brown; the solution is filtered, and the rutin is thrown down from the filtrate by an additional quantity of hydrated oxide of lead. The last pure yellow precipitate is decomposed with alcoholic hydrosulphuric acid, and the filtrate is freed from sulphide of lead, and evaporated to crystallisation (Stein).

Crystallised rutin (the properties of which see below) is rendered anhydrous by drying at a temperature of 150° to 160° (Zwenger & Dronke).

|	*Anhydrous.*		Zwenger & Dronke.
50 C	300	52·81	52·66
28 H	28	4·92	5·02
30 O	240	42·27	42·32
$C^{60}H^{28}O^{30}$	568	100·00	100·00

Rutin crystallised from acetic acid was once found to contain 53·70 p. c. C., and 490 H. (Stein). Stein afterwards supposed this rutin to have contained quercetin.

For rutin dried at 100° Borntrager gave the formula $C^{12}H^8O^8$, which was formerly adopted also by Rochleder & Illasiwetz and by Stein. Stein now supposes rutin, as well as quercetin, to contain equal numbers of atoms of hydrogen and oxygen, but gives for the former the formula $C^{14}H^{12}O^{12}$ or $C^{36}H^{24}O^{24}$, for the latter $C^{18}H^{10}O^{10}$. Since quercetin, $C^{20}H^7O^9$, according to Stein, contains more than 1 at. oxygen to each

at. hydrogen, there must be produced, by the splitting up of rutin (and of quercitrin), besides sugar and quercetin, a third body richer in oxygen, namely, formic acid. Moreover, the relation subsisting between quercetin and rutin is to be expressed, not by rutin + water = quercetin and sugar, but by quercetin + water = rutin and formic acid. — See also Ludwig on the formulæ of rutin, quercetin, &c. (*N. Br. Arch.* 112, 97).

Decompositions. 1. Rutin, after dehydration at 160°, cakes together at 190°, and then melts to a yellow viscid liquid, which, on cooling, solidifies to an amorphous mass, and takes up water when immersed in it. When more strongly heated, it is carbonised, emitting an odour of caramel, and yielding a distillate containing quercetin (Zwenger & Dronke). Rutin, melted at 180°, forms a yellow viscid liquid on cooling, and partly crystallises; at 220° a yellow sublimate is produced (Borntrager). Over a bath of oil of vitriol, rutin becomes coloured at 100°, melts at 120°, giving off gas-bubbles, boils at 200°, and is decomposed at 290°, yielding products of distillation. The water evolved at 200° over the oil-bath, contains formic acid; a solution of the melted mass in a little boiling water throws down amorphous quercetin on standing (Stein). — 2. *Nitric acid* boiled with rutin produces chiefly oxalic acid (Zwenger & Dronke); it forms picric acid, with a trace of oxalic acid (Stein). Cold nitric acid colours rutin yellow, then quickly olive, and at last red-brown (Stein). Hot nitric acid dissolves rutin, evolving gas, and decomposes it with red colour (Rochleder & Hlasiwetz). — 3. Rutin forms with *oil of vitriol* a brown yellow (olive-green, according to Rochleder & Hlasiwetz), afterwards brown-red solution, without liberation of sulphurous acid; water throws down from the solution, after an hour, olive-green flocks; after twelve hours, a violet precipitate; and the supernatant liquid, when evaporated and freed from sulphuric acid, yields very soluble crystals. The violet precipitate is free from sulphur, and dissolves in ammonia with yellowish colour, and in alcohol (Stein). — 4. When boiled with *dilute mineral acids*, rutin is split up into sugar (Stein) and quercetin (Hlasiwetz). The decomposition takes place with peculiar rapidity in an alcoholic solution; it is also effected by formic acid, especially at a temperature of 110°. When rutin is dissolved in boiling acetic acid of 60 p. c. and again crystallised, the amount of carbon in the crystals (dried at 120°) is increased to 51·8 or 52 p. c.; it now reduces copper solutions, and has, therefore, been partly converted into quercetin (Stein). — The decomposition is not effected by emulsin (Zwenger & Dronke). — From 100 parts of rutin dried at 100°, 39·24 to 43·25 parts (mean 41·9) of quercetin were obtained, corresponding to the equation:

$$C^{50}H^{28}O^{30} + 6HO = C^{26}H^{10}O^{12} + 2C^{12}H^{12}O^{12}.$$
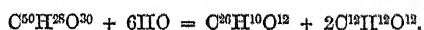
calculation 43 37 p. c. quercetin (Zwenger & Dronke).

Hlasiwetz (*Wien. Akad. Ber.* 17, 400) obtained 58·03 p. c. quercetin and 44·5 p. c. sugar. Stein formerly obtained, in presence of alcohol, 53·3 to 60·9 p. c. quercetin, in which case, however, the decomposition had proceeded too far, and the quercetin formed had been further altered, brown products and formic and acetic acids being produced; he afterwards decomposed rutin with dilute sulphuric acid in a sealed tube, and obtained, as the mean of eleven experiments, 47·5 p. c. quercetin, which was coloured brown by ulmin, and was still impure, but no longer contained rutin.

The *rutin-sugar* may be obtained, after removing the quercetin and sulphuric acid from the solution by evaporating, dissolving in alcohol,

and precipitating with ether, as a colourless, uncrystallisable syrup. It does not possess the property of rotating a ray of polarised light; it reduces cuprate of potash in the cold; yields, with boiling nitric acid, oxalic but no picric acid, and is not susceptible of fermentation (Zwenger & Dronke). The sugar obtained by Stein was impure and brown.

5. The easily formed solution of rutin in aqueous *alkalis* or *alkaline earths*, and especially in *ammonia*, acquires a dark-brown colour in the air, from absorption of oxygen (Bornträger, Rochleder & Hlasiwetz). By prolonged boiling of rutin with baryta-water, a brown solution is formed, which, when evaporated to dryness (the excess of baryta being first removed by carbonic acid), leaves a brown residue containing 32·4 p. c. C., 3·24 H., and 31·96 BaO (Stein). — 6. By the action of *sodium-amalgam* on an aqueous or alcoholic solution of rutin, paracarthamin (p. 493) is formed (Stein). — 7. Rutin does not reduce *cuprate of potash;* a few yellow flocks, free from cuprous oxide, are sometimes produced by prolonged boiling (Zwenger & Dronke). — 8. Rutin forms, with water and *oxide of silver*, a dark-red liquid, which leaves, on evaporation, an amorphous, brown residue containing 49·58 p. c. C., 4·51 H., and 45·91 O. (Stein). Rutin reduces *nitrate of silver* and *terchloride of gold* in the cold.

Combinations. *With Water.* — A. *With 4 at. water.* — Rutin dried at 100° contains 4 at. water (by calculation 5·96 p. c.; by experiment 5·63 and 5·92 p. c.), which is given off at 150° to 160° (Zwenger & Dronke).

	at 100°.				Bornträger. mean.		earlier. a.		Stein. mean. later.
50 C	300	....	49·66	....	50·31	....	50·85	....	50·06
32 H	32	....	5·29	....	5·55	....	5·55	....	5·65
34 O	272	....	45·05	....	44·14	....	43·60	....	44·29
$C^{50}H^{28}O^{30},4HO$	604	....	100·00	....	100·00	....	100·00	....	100·00

	Rochleder & Hlasiwetz.		Zwenger & Dronke. mean. a.		b.
50 C	50·15	....	49·57	....	49·14
32 H	5·70	....	5·42	....	5·52
34 O	44·15	....	45·01	....	45·04
$C^{50}H^{28}O^{30},4HO$	100·00	....	100·00	....	100·00

a was obtained from capers, *b* from rue.

B. *With 5 at. Water?* *Crystallised Rutin.* — Air-dried rutin contains from 1·61 to 2·12 p. c. more water than A, and loses it at 100° (1 at. = 1·47 p. c. HO) (Zwenger & Dronke). According to Stein, it loses 6·63 p. c. water at 100°, and has then the composition given under *a*; according to Bornträger, no water is expelled even at 180°.

Crystallised rutin forms pale yellow, delicate needles, having a somewhat silky lustre (Zwenger & Dronke). The needles are of a pure pale yellow colour, very thin, soft, and do not exhibit colours in polarised light (Stein). From water they are obtained white with a

tinge of sulphur-yellow; from alcohol pale sulphur-yellow. In-
odorous. Tasteless in the dry state and in aqueous solution; bitter
when dissolved in alcohol (Stein). Tastes slightly styptic, afterwards
saline (Zwenger & Dronke). Neutral; according to earlier statements
acid.—Rutin turns yellow in air containing ammonia (Rochleder &
Hlasiwetz). Impure rutin becomes greenish on exposure to light
(Stein).

C. *Aqueous solution.* Rutin is nearly insoluble in cold, but dissolves
easily in boiling *water,* with pale-yellow colour, which is destroyed by
acids; the rutin is rapidly deposited from the solution on cooling Zwenger
& Dronke). Crystallised rutin dissolves in 10941 parts (1094$\frac{1}{10}$? Kr.) of
cold, and 185 parts boiling water (Stein). The hot-saturated aqueous
solution (of impure rutin?) deposits crystals only after concentration
and standing for some days (Borntäger).
Rutin, digested with moderately dilute *mineral acids,* acquires a
lemon-yellow colour and is again rendered paler by water (Rochleder &
Hlasiwetz). On heating, it is dissolved and then decomposed.—
Rutin absorbs *hydrochloric acid gas* (Stein).
Rutin dissolves easily, with red-yellow colour (golden-yellow, ac-
cording to Stein) in aqeous *ammonia,* and is left free from ammonia on
evaporation (Borntäger).—It dissolves in *caustic alkalis* and their *car-
bonates* and in *baryta, strontia,* and *lime-water,* with yellow colour, without
forming crystallisable compounds; it is precipitated unaltered from
the solutions by acids (Borntäger). It expels carbonic acid from
aqueous carborate of soda, and hydrocyanic acid from ferricyanide of
potassium. With alcoholic soda, a garnet-red compound is formed
which, on keeping, turns brown and decomposes (Stein).— *Copper-
salts* and alcoholic *chloride of calcium* form precipitates with impure
rutin, but not with the pure substance (Zwenger & Dronke). *Alum*
and *stannate of soda* increase the solubility of rutin in water (Stein).

Lead-compound.—Alcoholic rutin is coloured a splendid golden-
yellow by a drop of solution of neutral acetate of lead (Stein).
Aqueous solutions are precipitated only by an excess of neutral
acetate; in alcoholic solutions, the precipitate is produced at once, and
contains a proportion of lead varying from 38·8 to 48·1 p. c. (Zwenger
& Dronke). The precipitate produced by an excess of neutral acetate
of lead contains 61·3 p. c. oxide of lead, but is orange-coloured at first
and afterwards chrome-yellow; alcoholic rutin converts the orange-
·coloured precipitate into the chrome-yellow, which contains 36·5 p. c.
oxide of lead (Stein).—The orange-yellow precipitate (chrome-yellow,
according to Rochleder & Hlasiwetz) thrown down from alcoholic rutin
by alcoholic neutral acetate of lead is free from carbonic and acetic
acids after washing (Borntäger).

				Borntäger.	Rochleder & Hlasiwetz.
50	C	300	29·52	30·29	28·72
28	H	28	2·76	2·49	3·09
30	O	210	23·63	20·19	23·57
4	PbO	448	44·09	47·03	44·62
$C^{50}H^{28}O^{30}$,4PbO		1016	100·00	100·00	100·00

Sesquichloride of iron colours aqueous rutin dark-green, becoming

red-brown when boiled. *Protochloride of iron* colours it brown-red to greenish (Zwenger & Dronke. Rochleder & Illasiwetz).

Rutin dissolves freely in hot *acetic acid* and is partially deposited on cooling (Rochleder & Illasiwetz). — It dissolves slightly in cold absolute *alcohol*, freely in boiling alcohol of 76 p. c. and crystallises only on concentration and addition of water (Bornträger. Rochleder & Illasiwetz). It dissolves in 359 parts of cold, and in 14·4 parts of boiling absolute alcohol.

When the alcoholic solution of rutin is evaporated the residue exhibits a brownish colour; and on precipitating an alcoholic solution of rutin with water, and evaporating the filtrate, there remains a brown, amorphous substance, the product of some change in the rutin (Stein).

Rutin is insoluble in boiling *ether*.

4. Robinin.

Zwenger & Dronke. *Ann. Pharm. Suppl.* 1, 257; *Lieb. Kopp's Jahresb.* 1861, 774.

Occurrence. In the blossoms of *Robinia pseudacacia.* Kümmell (*N. Br. Arch*, 93, 295) precipitated an aqueous decoction of the wood of *Robinia pseudacacia*, with basic acetate of lead. and obtained a yellow colouring matter which was separated from its lead-compound by sulphuric acid. The liquid freed from excess of sulphuric acid by means of carbonate of lead, throws down resin and tannic acid when concentrated, and on further evaporation, the colouring matter, which is soluble in water and ether, and coloured red-yellow by alkalis. This body, which was not further examined, was named by Kümmell, *Robiniin.*

Preparation. Fresh acacia flowers are boiled in water, and the decoction is again boiled six or eight times with fresh flowers; it is then evaporated to a syrup, which is repeatedly exhausted with boiling alcohol. The alcohol is distilled off, and the residue is set aside to crystallise. The crystals are pressed and washed with cold alcohol, to remove the greater part of the mother-liquor, then dissolved in boiling water, and neutral acetate of lead is added to the solution, whereby foreign substances are precipitated, while the robinin remains dissolved. The filtrate is freed from lead by hydrosulphuric acid, and evaporated, and the robinin thus obtained is purified by recrystallisation from water.

Properties. (See crystallised robinin). Robinin loses its water of crystallisation at 100°, and becomes anhydrous. It melts partially at 190°, completely at 195°, to a yellow liquid, which solidifies to an amorphous mass on cooling. Neutral. Tasteless in the solid form; slightly styptic in aqueous solution.

Dried.				Zwenger & Dronke. mean.
50 C	300		51·19	50·98
30 H	30		5·10	5·51
32 O	256		43·71	43·51
$C^{50}H^{30}O^{32}$	586		100·00	100·00

The correctness of this formula is dependent upon that of quercetin. (See page 492.)

Decompositions. 1. By *dry distillation*, robinin yields a yellow distillate, containing quercetin in solution. — 2. When heated above its melting-point, it *burns* with a smoky flame and a smell of burnt sugar, and leaves charcoal. — 3. It is decomposed by concentrated *nitric acid* (with peculiar facility by the fuming acid), with formation of oxalic acid and a large quantity of picric acid. — 4. When heated with *dilute acids*, it very readily splits up into quercetin and robinin-sugar :

$$C^{50}H^{30}O^{32} + 4HO = C^{26}H^{10}O^{13} + 2C^{12}H^{12}O^{12}.$$
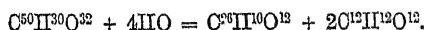
100 parts of crystallised robinin yield 37·96 parts of quercetin, dried at 100° (by calculation 38·25 parts).

Robinin-sugar, separated in the same manner as quercitrin sugar, as described at page 348, vol. xv., does not crystallise, but is obtained as a sweet, brown syrup, which smells like caramel when heated, and yields with nitric acid a large quantity of picric acid, together with traces of oxalic acid. It reduces cuprate of potash in the cold. Does not undergo fermentation with beer-yeast.

5. Robinin reduces boiling *cuprate of potash* and *chloride of gold* quickly ; *nitrate of silver* slowly and incompletely. — 6. It is not altered by *emulsin*.

Combinations. — *With Water.* — *Crystallised Robinin.* — Fused robinin takes up water when immersed in it. — Very delicate straw-yellow needles, having a slightly silky lustre. They lose 14·46 to 14·61 p. c. water at 100° (calculation for 11 at. = 14·45 p. c.).

|	*Crystallised.*			Zwenger & Dronke. *mean.*
50 C	300	....	13·79	43·50
41 H	41	....	5·98	6·33
43 O	344	....	50·23	50·17
$C^{50}H^{30}O^{32}$ + 11aq.	685	....	100·00	100·00

Robinin dissolves slightly in cold, and freely in boiling water. The bright yellow solution is decolorised by acids.

Aqueous *ammonia* and the *caustic alkalis* and their *carbonates* quickly dissolve robinin with golden-yellow colour. The solution in ammonia turns brown on standing, but not that in the fixed alkalis.

An aqueous solution of robinin does not precipitate *metallic salts*. It colours *sesquichloride of iron* dark-brown or greenish, but does not affect *protochloride of iron*.

Robinin does not precipitate aqueous *neutral acetate of lead*, but produces in an alcoholic solution, a precipitate soluble in warm water or alcohol. — With an excess of *basic acetate of lead*, it forms a yellow precipitate.

Robinin dissolves slightly in cold *alcohol*, and more easily in boiling alcohol containing water. — It is insoluble in *ether*.

B. *Crocetin and Crocin.*

Crocetin.

? $C^{34}H^{23}O^{11}$.
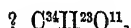
ROCHLEDER & L. MAYER. *Wien Acad. Ber.* 29, 5.

When crocin (see below) is heated with dilute hydrochloric or sulphuric acid in a stream of hydrogen or carbonic acid, crocetin is precipitated, whilst crocin-sugar remains in solution. The separated crocetin is collected, washed, and dried in a vacuum over oil of vitriol.

Dark-red, amorphous powder.

Calculation, according to Rochleder & Mayer.					L. Mayer. mean.
34 C	204		61·76		61 45
23 H	23		7·30		7 39
11 O	88		27·94		28·16
$C^{34}H^{23}O^{11}$	315		100 00		100·00

The formulæ $C^{18}H^{12}O^6$ and $C^{32}H^{22}O^{10}$ also agree approximately with the analysis (Kr.).

Decompositions. An aqueous solution absorbs *oxygen* easily from the air, and forms products containing a smaller proportion of hydrogen. — Crocetin is coloured blue by *oil of vitriol.*

Crocetin is slightly soluble in *water.* It precipitates lead-salts lemon-yellow. Dissolves easily in *alcohol* and *ether.* It dyes cloth prepared with tin-mordants, on boiling, a dirty green-yellow colour, turning bright golden-yellow in ammoniacal water, and unaltered by light or soap.

Glucoside of Crocetin.

Crocin.

B. QUADRAT. *Wien. Akad. Ber.* 6, 543; *J. pr. Chem.* 56, 68; abstr. *Ann. Pharm.* 80, 340; *Pharm. Centr.* 1852, 411; *Lieb. Kopp's Jahresb.* 1851, 532.

v. ORTH. *Wien. Akad. Ber.* 13, 511; *J. pr. Chem.* 64, 10; *Pharm. Centr.* 1854, 897; *Lieb. Kopp's Jahresb.* 1854, 663.

ROCHLEDER & MAYER. *Wien. Akad. Ber.* 29, 3; *J. pr Chem.* 74, 1; *Lieb. Kopp's Jahresb.* 1858, 475; Prelim. notice: *Wien Akad. Ber.* 24, 41; *J. pr. Chem.* 72, 394.

Polychroite. — The yellow colouring matter of saffron (Quadrat) and of Chinese yellow pods, the fruit of *Gardenia grandiflora* (Rochleder & Mayer). Occurs also in *Fabiana indica* (Filhol, *Compt. rend.* 50, 1184).

Extracts were formerly prepared by exhausting the aqueous extract of saffron with alcohol and evaporating; their behaviour was described by Bouillon-Lagrange & Vogel (*Ann. Chim.* 80, 198), Johnson (*Thoms. Ann.* 13, 388), and N. E. Henry (*J. Pharm.* 7, 399). —Stein (*J. pr. Chem.* 48, 329) had already obtained the colouring matter from the Chinese yellow pods of commerce (*Wongshu*) by a process similar to that of Rochleder & Mayer, and found it to be free from nitrogen, insoluble in water, and soluble in alkalis.

The Decamalee gum of Scinde, which is obtained from *Gardenia lucida*, contains, according to Stenhouse (*Chem. Soc. Qu. J.* 9, 238; *Ann. Pharm.* 98, 316; *Lieb. Kopp's Jahresb.* 1856, 631), a crystallisable ingredient, *Gardenin*, which Rochleder (perhaps erroneously, Kr.) regards as crocin. —An extract of the gum prepared with strong alcohol throws down yellow flocks on cooling, and after removing these and evaporating the filtrate in a vacuum, the gardenin is deposited in thin golden-yellow crystals, sometimes half an inch long, and having a shining fracture. With nitric acid it forms picric but no oxalic acid; it is insoluble in water, ammonia, and the fixed alkalis, but dissolves in hot hydrochloric or sulphuric acid, and is precipitated by water. It is moderately soluble in alcohol, and is not precipitated therefrom by basic acetate of lead, or by ammoniacal nitrate of silver. It dissolves in ether.

Preparation of Crocin. 1. *From Saffron.* Saffron is freed from fat by ether and afterwards boiled with water. The aqueous decoction is precipitated with basic acetate of lead; and the lead-salt is washed and decomposed by hydrosulphuric acid, whereupon the crocin is taken up and retained by the sulphide of lead, and may be afterwards dissolved out by boiling the sulphide in alcohol. The alcoholic solution is concentrated over the water-bath, filtered from the deposited sulphur, and evaporated to dryness (Quadrat). A partial decomposition of the crocin takes place on evaporating the alcoholic extract (Rochleder).

2. From *Yellow pods.* — The crushed pods are boiled with alcohol, and the decoction is strained and filtered. The alcohol is distilled off over the water-bath, and a black-green substance, which separates from the aqueous residue, is removed by passing the liquid through a wet filter. The filtrate is then diluted; moist hydrate of alumina is added; and, after standing for some days, the liquid is filtered from the deposit of alumina, which contains the whole of the tannic acid, and precipitated with basic acetate of lead. The fine orange-coloured precipitate is rapidly washed, suspended in water, and decomposed by hydrosulphuric acid. The sulphide of lead is thoroughly washed with water and afterwards boiled in alcohol; the alcoholic solution is evaporated in a vacuum over oil of vitriol; and the residue, dissolved in the least possible quantity of water, is filtered from sulphur and again evaporated in a vacuum (Rochleder & Mayer).

Properties. Roseate (Quadrat), splendid red powder (Rochleder & Mayer). Inodorous; altered by light, only after very long exposure (Quadrat).
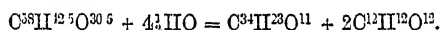
Calculation according to Rochleder.			Quadrat. at 100°.		Mayer. mean. in vacuo.
58 C	348·0	....	51·85	... .	54·81
42½ H	42·5	....	6·70	....	6·73
30¼ O	241·0	....	38·15	... .	38·46
$C^{58}H^{42}O^{30}$ + ½HO	634·5	....	100·00	.. ..	100·00

The above is according to Rochleder: Quadrat's formula is $C^{20}H^{13}O^{11}$. —The formulæ $C^{56}H^{42}O^{30}$ (calc. 54·37 C., 6·79 H.) and $C^{40}H^{22}O^{16}$ (calc. 54·54 C., 6·66 H.)

likewise agree with Mayer's analysis: according to these formulæ, however, the decomposition of crocin by hydrochloric acid ($C^{56}H^{42}O^{30}$ + 4HO = $C^{32}H^{22}O^{10}$ + $2C^{12}H^{12}O^{12}$ or $C^{30}H^{20}O^{16}$ + 2HO = $C^{18}H^{13}O^{6}$ + $C^{12}H^{12}O^{12}$) should yield 58 2 or 54·5 p. c. sugar and 47·5 or 50·9 p. c. crocetin. See below. (Kr.)

In preparing the tannic acids from yellow pods (xv. 520) v. Orth formerly obtained a resinous red-yellow colouring matter containing 61·55 p. c. C., 6·66 H., and a yellow amorphous colouring matter containing, after deducting 10·9 p. c. ash, 50·57 p. c. C., 7·35 H., both substances being dried at 100°.

Decompositions. 1. Crocin turns black-brown at 120°, puffs up at 180°, and is completely decomposed at 200° (Quadrat).—2. When heated with dilute *hydrochloric* or *sulphuric acid*, it splits up into crocetin and a peculiar sugar, both of which undergo rapid alteration in the air (Rochleder & Mayer). Highly concentrated solutions of crocin throw down, on addition of acids, a quantity of crocetin, amounting to 41 p. c. of the crocin; the sugar remaining in solution throws down from an alkaline solution of cupric oxide, a quantity of cuprous oxide corresponding to 27·94 to 28·5 p. c. grape-sugar, or to double that quantity of crocin-sugar :

$$C^{38}H^{12\,5}O^{30\,6} + 4\tfrac{1}{2}HO = C^{34}H^{23}O^{11} + 2C^{12}H^{12}O^{12}.$$

by calculation 56·7 p. c. sugar, 49·6 p. c. crocetin (Rochleder & Mayer), — Crocin is altered by concentrated acids; *nitric acid* colours it green, *oil of vitriol* blue (indigo-blue, then violet, according to Rochleder & Mayer), *hydrochloric acid* black-brown. *Tartaric, tannic,* and *gallic acids* throw down red flocks from aqueous solutions (Quadrat).— 3. Crocin is decomposed by strong aqueous *alkalis*, with formation of a volatile neutral oil, which differs from saffron in smell and is lighter than water, but changes after some time to a brown mass, sinking in water (Quadrat).

Crocin dissolves in *water* with yellow (Quadrat), *yellow-red* colour (Rochleder & Mayer). Traces of alkali increase its solubility. (Quadrat.)

Dilute *alkalis* dissolve crocin, and form with it saline compounds soluble in water, with yellow colour (Quadrat.) Aqueous crocin is precipitated yellow by baryta- and lime-water, green by cupric-salts.

Lead-compound.—Aqueous crocin precipitates lead-salts orange-red (Rochleder and Mayer.)—An aqueous solution of crocin is precipitated by basic acetate of lead, and the red precipitate is washed and dried at 100° (Quadrat).

Approximate calculation, according to Rochleder.				Quadrat.
58 C	348		21·01	21·81
44 H	44		2 65	2·31
32 O	256		15·16	15 92
9 PbO	1008		60 88	59 96
$C^{58}H^{42}O^{30}$,9PbO + 2aq.	1656		100·00	100·00
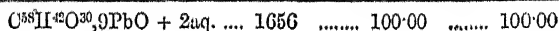
According to Quadrat, $C^{20}H^{13}O^{11}$,3PbO.

Crocin dissolves very readily in *alcohol*, very slowly in *ether*.

C. *Ilixanthin, Ilicic Acid, and Ilicin.*

Ilixanthin.

$C^{34}H^{22}O^{22}$.
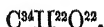
MOLDENHAUER (1857). *Ann. Pharm.* 102, 346; abstr. *J. pr. Chem.* 71, 440; *Chem. Centr.* 1857, 766.

Occurrence. In the leaves of *Ilex aquifolium.* The leaves gathered in January contain scarcely any ilixanthin, while those gathered in August contain a large quantity.

The colouring matter of the common buckwheat (*Polygonum fagopyrum*) forms small yellow needles, having the composition $C^{8}H^{2}O^{2}$ (calc. 50 p. c. C., 5·6 H.), and otherwise resembling rutin (p. 500) or ilixanthin. It is coloured dark-orange by hydrochloric or sulphuric acid, and is decolorised by a large quantity of water; with nitric acid it forms oxalic acid. — It is slightly soluble in cold, and more easily soluble in boiling water. It dissolves in alkalis, with dark-yellow colour, and is precipitated from the solution by acids. The alkaline solution decomposes in the air. — Neutral acetate of lead forms with it a chrome-yellow compound. Dissolves easily in alcohol (Schunck, *Chem. Gaz.* 1858, 18; *Dingl.* 147, 465; *Lieb. Kopp's. Jahresb.* 1857, 489). Grothe (*N. Br. Arch.* 115, 85) regards this colouring substance as chrysophanic acid (p. 171).

Preparation of Ilixanthin. The leaves are exhausted with alcohol of 80 p. c.; the tincture thus obtained is freed from the greater part of the alcohol by distillation, and the residue is set aside to crystallise. The granules, which separate after some days, are dried, washed with ether to remove the green colouring matter of the leaves, dissolved in alcohol, and again separated by evaporation and addition of water; they are lastly recrystallised from hot water. A further quantity of ilixanthin may be obtained from the mother-liquor by reducing it to a syrup, dissolving in absolute alcohol, evaporating the alcoholic solution, dissolving the residue in water, and precipitating with basic acetate of lead. The washed precipitate is decomposed under hot water with hydrosulphuric acid, and the filtrate is evaporated to a syrup, whereupon the ilixanthin crystallises out.

Properties. Straw-yellow microscopic needles, which melt at 198° to transparent red-yellow drops. Contains no nitrogen.

					Moldenhauer.
34 C	204		50·75	.. ...	50·39
22 H	22		5·47	.. ...	5 61
22 O	176		43·78	.. ..	43·97
$C^{34}H^{22}O^{22}$	402		100·00		100 00

Decompositions. Ilixanthin boils and decomposes at 215°. — It does not reduce an alkaline solution of *cupric oxide*, even on prolonged boiling. Ilixanthin is nearly insoluble in cold *water*, but dissolves easily

in hot water, with yellow colour. — It dissolves in warm concentrated *hydrochloric* acid. — The aqueous solution is coloured yellow by *caustic alkalis* or their *carbonates;* it becomes colourless on addition of *sulphuric acid*, but does not undergo further change even when boiled. — *Ferrous* and *cupric salts* do not affect ilixanthin; aqueous *sesquichloride of iron* colours it grass-green. — *Neutral* or *basic acetate of lead* produces in the aqueous solution a splendid yellow precipitate, dissolving without colour in acetic acid.

Ilixanthin is soluble in *alcohol*, insoluble in *ether*. It dyes cloth prepared with alumina or iron mordants, yellow.

Ilicic Acid.

MOULDENHAUER. *Ann. Pharm.* 102, 350; *J. pr. Chem.* 71, 440.

In *Ilex aquifolium*. The leaves gathered in January contain gum, or a similar substance, which renders the preparation of the acid difficult. — Known only in combination with bases. — An aqueous decoction of the leaves is precipitated with basic acetate of lead; the filtrate, freed from lead by hydrosulphuric acid, is heated with hydrated oxide of lead; the dissolved lead is again removed by hydrosulphuric acid; and the filtrate is reduced to a syrup. The laminæ formed after some days, are purified by pressing, dissolving in water, precipitating with alcohol, and recrystallising with the help of animal charcoal, whereby colourless ilicate of lime is obtained.

Ilicate of lime contains 18 p. c. lime, and is readily soluble in water, but insoluble in alcohol. An aqueous solution does not precipitate salts of *manganese, zinc, iron, copper,* or *silver,* but produces a precipitate with *protochloride of tin,* and the *neutral* and *basic acetates of lead*. When the lead-salts are decomposed by hydrosulphuric acid, a colourless syrup is formed, which still contains lime, and, by neutralisation with carbonate of baryta, yields amorphous ilicate of baryta.

Ilicin.

The bitter principle of *Ilex aquifolium* (*Handbuch*. viii, *Phytochem.* 22). — According to Déleschamps (*Répert.* 41, 230), the decoction of the leaves is precipitated with basic acetate of lead; carbonate of potash is added to make the liquid filter, and to precipitate any excess of the lead-salt; and the filtrate is acidified with dilute sulphuric acid, again filtered, saturated with carbonate of lime, and evaporated to a syrup. Alcohol extracts from the syrup a light brown, very hygroscopic substance, which, in thin layers, dries up to small, shining scales. — Or, the aqueous extract is exhausted with alcohol, the alcoholic solution evaporated, and the dry residue exhausted with water at 40°. The filtrate is precipitated with basic acetate of lead, freed from excess of lead by hydrosulphuric acid, evaporated, and treated with alcohol, which takes up the ilicin, and leaves it behind on evaporation. — The aqueous solution of the alcoholic extract may also be treated, as above, with acetate of lead, dilute sulphuric acid, and carbonate of lime in succession, the filtrate evaporated, and the ilicin extracted

from the residue by alcohol. — Bitter, amorphous, brown, very hygroscopic mass (still containing a little potash), converted by acids at a gentle heat into a black substance, with empyreumatic odour. — It is soluble in water and alcohol, insoluble in ether.   Lebourdin (*N. Ann. Phys.* 24, 62 ; *Ann. Pharm.* 67, 251), agitates the decoction of the leaves with animal charcoal, then heats it therewith to boiling; leaves it to cool; removes the now colourless and tasteless liquid, washes the charcoal with cold water, and boils it with alcohol; and leaves the filtrate to evaporate; it then leaves a colourless, very bitter syrup, and finally an amorphous, neutral jelly, easily soluble in water and in alcohol. — Moldenhauer's ilicin (*Ann. Pharm.* 102, 352) appears also to be different from this.   Moldenhauer removes the alcohol from the alcoholic extract of the leaves by distillation, and the separated resin by filtration ; precipitates with basic acetate of lead ; washes the yellow precipitate; and decomposes it under water with hydrosulphuric acid.   The sulphide of lead, after being well boiled with water, yields the ilicin to alcohol, as a very bitter, dark brown substance, resembling tannin, and slightly in water. — Bennemann (*N. Br. Arch.* 93, 4) gives the name of ilicin to crystals which he obtains as follows :—He precipitates the decoction with basic acetate of lead; decomposes the washed precipitate under water with hydrosulphuric acid; filters the liquid from the sulphide of lead ; and evaporates to dryness.   By repeatedly exhausting the residue with alcohol, and leaving the solution to evaporate, needles were finally obtained, but not in sufficient quantity for further examination.

D. Spiræa-yellow.

Löwig & Weidmann.   *J. pr. Chem.* 19, 236.

Yellow of the flowers of Spiræa ulmaria.   Spiræaïn.   The flowers are exhausted with ether ; the ether is distilled off from the yellow tincture; and the residue is mixed with warm water, which throws down an impure colouring matter, while a brownish-green oil floats upon the surface.   This oil is removed ; the colouring matter is dissolved in hot alcohol; the fat which separates on cooling is also removed; and the liquid is evaporated to dryness, whereupon the yellow remains, and may be further purified by repeating the process.

Yellow powder made up of fine needles.   The alcoholic solution slightly reddens litmus. — Contains, at 120°, on the average, 58·27 p. c. carbon, 5·23 hydrogen, and 36·50 oxygen, answering, according to Löwig & Weidmann, to the formula $C^{15}H^3O^7$.

Decomposed by *heat.* — Not attacked by cold *nitric acid;* but hot (or fuming) nitric acid dissolves it, with slight evolution of gas, forming a red solution, from which it is precipitated by water, for the most part unaltered.   The red solution when boiled loses its colour, is no longer precipitable by water, and leaves on evaporation a light yellow acid mass. — Distilled with *peroxide of manganese* and *sulphuric acid,* it yields carbonic and formic acids. — With *bromine,* it gives off a large quantity of hydrobromic acid, and forms an orange-yellow mixture of several compounds.

Insoluble in *water*, dissolves with a deep yellow colour in *oil of vitriol*, and is precipitated undecomposed by water. On heating the solution, decomposition takes place. Insoluble in cold, sparingly soluble in boiling *hydrochloric acid.*

Dissolves with yellow colour in *potash, ammonia,* and *carbonate of potash,* expelling carbonic acid from the latter when heated, and is precipitated unchanged by hydrochloric acid. The alkaline solutions turn brown when exposed to the air. An alcoholic solution of spiræa-yellow is precipitated yellow by sulphate of alumina, lemon-yellow by tartar-emetic, carmine-red by neutral acetate of lead, the precipitate blackening when dried; dark green by ferrous, black by ferric salts; no precipitate with mercuric, auric, or platinic chloride. With nitrate of silver, on addition of ammonia, it forms a black precipitate insoluble in ammonia.

Lead-salt. — Precipitated from the alcoholic solution by excess of alcoholic sugar-of-lead; purified by washing with water and with alcohol. After drying at 120°, it contains, on the average, 58·23 p. c. lead-oxide, 24·2 carbon, and 1·90 hydrogen.

Spiræa-yellow dissolves in *alcohol* and in *ether*, with dark green colour, changing to yellow on dilution. It does not precipitate *tannin.*

SECOND APPENDIX TO COMPOUNDS CONTAINING 34 AT. CARBON.

A. Yellow Colouring Matters.

1. Yellow of Flowers.

MARQUART. *Die Farben der Blüthen.* Bonn, 1835.
FRÉMY & CLOEZ. *N. J. Pharm.* 25, 249; *J. pr. Chem.* 62, 269.
FILHOL. *Compt. rend.* 39, 194; *J. pr. Chem.* 63, 78; *Compt. rend.* 50, 545 and 1182.

The various colours of flowers may be formed, either from colouring matters peculiar to each individual species, or by a small number of more widely diffused colouring matters, and their mixtures one with the other. Such diffused colouring matters are, according to Marquart:—1. *Anthoxanthin,* or yellow of flowers; 2 *Anthocyan,* or blue of flowers; 3. A colourless *Extractive Matter,* which is turned yellow by alkalis; and 4. *Resin of flowers.* The insoluble substance, called *Xanthin* by Frémy & Cloez, appears to correspond with Marquart's anthoxanthin; their *Xantheïn,* soluble in water, with Marquart's colourless extractive matter; and their *Cyanin* with his anthocyan. — See also Martens (*Institut.* 1855, p. 168).

Anthoxanthin, according to Marquart, is formed from chlorophyll by assumption, anthocyan by elimination of water; the resin of flowers may be regarded as chlorophyll which has been deprived of a certain quantity of water, but not sufficient to convert it into anthocyan·

The yellow of flowers (*xanthin*) of Frémy & Cloez, which is insoluble in water, is not capable by itself of producing either red, blue, or green colours. It is extracted by boiling alcohol from *Helianthus annuus,* and

is deposited almost entirely on cooling, but mixed with oil, which may be removed by heating with a small quantity of alkali, decomposing with an acid, and extracting the resulting fatty acid with cold alcohol. It is of a fine yellow colour, amorphous and resinous; insoluble in water, but soluble, with gold-yellow colour, in alcohol and in ether.

Marquart's *anthoxanthin*, obtained from different plants, exhibits different reactions with solvents, but the same in all cases with precipitating and colouring reagents. It is generally extracted by cold alcohol of 85 p.c., from fresh yellow flowers, after they have been freed from calyx, stamens, and pistil; from some flowers, however, as those of *Cassia ligustrina*, it can be extracted only by absolute alcohol or ether; in others, again (*Crocus mœsiacus, Papaver nudicaule*), it appears to be soluble in water.—The yellow tinctures, when evaporated, leave a mixture of anthoxanthin and colourless extractive matter, from which water takes up the latter, leaving anthoxanthin undissolved. It exhibits the following properties : It is decolorised by chlorine, coloured olive-green by ferric salts, not altered by infusion of galls or solution of gelatin. Oil of vitriol colours it dark indigo-blue, the colour passing into purple-red and disappearing on addition of water. Hydrochloric acid colours it green at first, then blue, and alcohol then dissolves the whole, forming a blue solution. It is insoluble in water, and is but slightly dissolved by ammonia, potash, or carbonate of potash. Ether, volatile oils, and fixed oils, dissolve it in all proportions; alcohol of 86 p. c. less easily.

Filhol mentions, as identical with Marquart's anthoxanthin, a colouring matter of flowers, to which he ascribes the following properties : It is turned blue both by oil of vitriol and by nitric acid, but the colour quickly disappears. Dilute hydrochloric acid gradually imparts to its alcoholic solution a fine greenish-blue colour; the concentrated acid immediately turns it green; and the solution, which turns yellow in contact with the air, deposits a black precipitate, soluble, with greenish-blue colour, in water and in alcohol. By Frémy's process anthoxanthin may, like chlorophyll, be separated into a blue and a yellow colouring matter (see *Chlorophyll*) (Filhol).

The yellow of flowers is not bleached or altered in any way by sulphurous acid (Schönbein, *J. pr. Chem.* 53, 331).

The yellow of flowers, or *xanthein* of Frémy and Cloez, which is soluble in water, is extracted, by alcohol, together with fat and resin, from yellow dahlias. The solution is evaporated; the extract exhausted with water; the aqueous solution likewise evaporated; the residue drenched with absolute alcohol; the alcoholic solution diluted with water and precipitated by neutral acetate of lead; and the precipitate immediately decomposed by sulphuric acid, whereupon the xanthein passes into the solution. It is amorphous, turns brown with alkalis, but the colour is rendered paler by addition of acids. It dyes fabrics bright-yellow, forms brown and yellow lakes, and dissolves in water, alcohol, and ether.

Marquart finds in yellow flowers a *colourless extractive matter*, which is coloured yellow by alkalis, even when very dilute. It is extracted by water from the alcoholic extract of such yellow flowers as contain anthoxanthin insoluble in water, best from the extract of *Narcissus Tazetta, Arctotis grandiflora*, or *Cassia ligustrina*. The aqueous solution of this substance is colourless, especially if a small quantity of free acid is present; it is coloured by boracic acid in the same manner as

by alkalis, yellow by neutral acetate of lead ; it is not altered by alum or protochloride of tin. Oil of vitriol colours it yellow ; dilute acids decolorise the solution which has been turned yellow by alkalis. This colourless extractive matter occurs likewise in white flowers, together with resin of flowers, and is the cause of their being turned yellow by alkalis (Marquart).

All white flowers likewise contain a white or yellowish resin, Marquart's *resin of flowers*, which is likewise found in coloured flowers. It dissolves in oil of vitriol with brown colour, which, in an open vessel, quickly changes to dark purple-red, from absorption of water. The alcoholic solution of the flower-resin has but little colour, and is not acid ; it is but slightly altered by neutral acetate of lead or ferric hydrochlorate. The flower-resin dissolves in ether, less easily in oil of turpentine and in fixed oils (Marquart).

Filhol describes, as identical with Marquart's flower-resin and related to luteolin (xv. 28), an amorphous light greenish-yellow substance, existing in flowers, and in green, but not in blanched parts of plants ; also in fruits, but only as a trace in mosses. It is not volatile. It dissolves in water, alcohol, and ether, being colourless in acid, yellow in alkaline solutions. With concentrated hydrochloric acid, it assumes a fine yellow colour, which disappears on addition of water. It is to this substance that, in Filhol's opinion, must be attributed the fact that white flowers and the white parts of variegated flowers, are coloured permanently yellow by ammonia, and decolorised again by acids.

2. Resinous Yellow of Leaves.

Chromule jaune of Macaire-Princep, *Xanthophyll of* Berzelius.

Many leaves, especially those of *Betula alba, Pyrus communis, Pyrus malus, Ulmus campestris,* and *Fraxinus excelsior,* turn yellow after frosty nights in autumn, before they fall. Other leaves turn brown, in consequence of a change not connected with that just mentioned (Berzelius) ; according to Chatin & Filhol (*Compt. rend.* 57, 39), from the presence of a colourless substance, abundant in flowers and in quickly growing tissues, which turns brown by absorption of oxygen.

According to Macaire-Princep (*Ann. Chim. Phys.* 38, 415 ; *Pogg.* 14, 516) the autumnal colours arise from the foliage ceasing to eliminate oxygen, and on the other hand beginning to absorb it from the air and form an acid, which produces the red and yellow colours, and after whose removal by alkalis, the green colour is restored. Neither L. Gmelin (*ed.* 3, II, 633) nor Berzelius has found these statements correct ; according to the latter, leaves which have been turned yellow cannot be turned green again ; and if this effect can be produced with red leaves, it is only because the alkali forms a green compound with the red colouring matter. See also Hugo Mohl. (*Flora,* 1837, Nov., Dec), *N. Ann. Sc. Nat. Bot. N.* 9, 212 ; Robinet & Guibourt (*J. Chim. méd.* 3, 161) ; Ronchas (*J. Chim méd.* 10, 32).

When leaves turn yellow in autumn, the change is due to a peculiar yellow colouring matter, which previously existed in the green leaves, together with chlorophyll ; it may be extracted by water, but is insoluble in alcohol ; forms beautiful siskin-yellow lakes ; and is different from that which exists in plants, which, like wheat, &c., turn

yellow only later in the season, or after drying (*J. Chim. méd.* 3, 161).
—Leaves which turn yellow in autumn contain only phylloxanthin
(see below), which exists in them before the phyllocyanin, and lasts
longer than the latter (Frémy, *Compt. rend.* 50, 411).—According to
Ferrein, the yellow colouring matter is xanthotannic acid (xv. 533).
According to Phipson (*Compt. rend.* 47, 912), it is related to frangulin
(p. 76); yellow leaves drenched with oil of vitriol assume the same
green colour as frangulin when similarly treated; green leaves first
turn yellow; then, if the action of the oil of vitriol be continued, they
also become emerald-green, and a few seconds later, brown.— Stein
regards the yellow of autumnal leaves as rutin, or a substance allied
thereto ; also the yellow colouring matters of straw and of *Æthalium
flavum* (see below).

From the yellow-turned leaves of *Populus fastigiata* warm ether
extracts wax and fat; boiling alcohol extracts the colouring matter, and
leaves it on evaporation, as a solid, orange-yellow, translucent mass. It
is coloured by aqueous alkalis, slowly in the cold, quickly when heated,
of a fine green, being in fact converted into chlorophyll. It is in-
soluble in water, easily soluble in alcohol, insoluble in oils (Macaire-
Princep). The accuracy of these statements is doubted, but not from experiments
upon the same plant (Kr.).

The leaf-yellow of Berzelius is extracted by cold alcohol of sp. gr.
0·833 from the freshly gathered leaves of *Pyrus communis*, and sepa-
rates, after the alcohol has been distilled off, either in grains or as a
yellow layer floating on the surface. It contains fats, which can only
be partially extracted by digestion with weak potash-ley and cold
alcohol, and remains after this treatment, as a greasy-yellow mass
melting at 46°, and intermediate, as it were, between oil and resin.
It bleaches when exposed to light in contact with water; dissolves
slowly (even after bleaching) in alcohol, and sparingly in potash-ley,
and is precipitated by acids in neutral flocks. This leaf-yellow can
neither be produced from chlorophyll nor converted into it (Berzelius,
Ann. Pharm. 21, 257).

Leaves turned yellow in autumn are reddened by immersion in am-
moniacal ether, but recover their yellow colour in aqueous sulphurous
acid and other reducing liquids ; leaves reddened in autumn also turn
yellow when immersed in the same liquids (Chatin & Filhol).

If an alcoholic extract prepared in the cold from the fresh leaves of
Polygonum tinctorium, be exhausted with ether, and the ether evapo-
rated, leaf-yellow remains as a pure yellow, neutral, bitter mass, which
makes resinous spots on paper. It is insoluble in water, nearly in-
soluble in ammonia and potash, which are slightly coloured by it ; more
easily in alcohol and in ether. It is gradually decolorised by chlorine
and nitric acid, turned green by oil of vitriol, and appears to be a pro-
duct of the transformation of chlorophyll, resulting from the action of
ether, inasmuch as solutions of chlorophyll in ether and oil of turpen-
tine also soon turn yellow. (Hervey, *J. Pharm.* 26, 293 and 301).

The reddish yellow decoction of the green leaves of *Vitis vinifera*
deposits a sediment when left at rest, and the liquid filtered from this
assumes a light lemon-yellow colour when treated with potash. Neu-
tral acetate of lead then throws down a precipitate of a fine chrome-
yellow colour. This colouring matter is likewise obtained from the
green leaves of the black-grape vine (Legrip, *J. Chim. méd.* 23, 190).

The following yellow colouring matters cannot with certainty be classed with any known compounds of that group.

The colouring matter of *Aethalium flavum* is extracted by absolute alcohol. It is uncrystallisable, deep yellow, permanent, and does not turn ferric hydrochlorate green. Its lead-compound contains 13·85 p. c. carbon, 1·37 hydrogen, 12·94 oxygen, and 71·84 lead-oxide (Stein).

The colouring matter of *Cocculus indicus* is lemon-yellow, transparent, bitter from the presence of picrotoxine, soluble in water and in alcohol, insoluble in ether ; not precipitable by neutral acetate of lead (Boullay, *Bull. Pharm.* 4, 24).

The flower of *Cytisus Laburnum*, after exhaustion with ether, gives up its yellow to boiling alcohol. This colouring matter is soluble in water, alcohol and ether, decomposible by acids, and becomes darker-coloured when treated with alkalis (Caventou, *J. Pharm.* 3, 301).

Flavequisetin is the name given by Baup (*Ann. Pharm.* 77, 295) to a yellow colouring matter from *Equisetum fluviatile.* When the juice of the plant from which the chlorophyll has separated, is mixed with neutral acetate of lead, and the precipitated malate and aconitate of lead are filtered off, the filtrate yields, with basic acetate of lead, an abundant yellow precipitate, which, when decomposed by sulphuric acid, yields an uncrystallisable acid and blackish grains. The latter dissolve sparingly in ether and in cold water, separate from the hot aqueous solution in beautiful yellow flakes, from the easily formed alcoholic solution in crystals, and impart a fine yellow colour to mordanted cotton.

From the aqueous extract of the stalks and flowers of *Silene nutans*, basic acetate of lead throws down a copious yellow precipitate, which gives up its colouring matter to ammonia. The ammoniacal solution when carefully concentrated and set aside for two or three days, deposits a white powder, sparingly soluble without colour in water, abundantly and with yellow colour in ammonia. This colouring matter is very widely diffused (Malapert, *J. Chim. méd.* 23, 238).

The yellow of the flowers of *Tropæolum majus* dissolves readily in water and in alcohol, with brownish colour, passing into cherry-red. Its aqueous solution is coloured deep cherry-red by acids, dirty brown-green by carbonate of soda, and forms yellow and red precipitates with heavy metallic salts (John, *Chem. Schr.* 4, 112).

The colouring matter of *straw* is pale yellow, amorphous, easily alterable, and does not colour ferric hydrochlorate green. Its lead-compound, purified by repeated fractional precipitation with basic acetate of lead, contains, on the average, 31·93 p. c. C., 3·15 H., 26·77 O., and 38·58 PbO. (Stein).

The alcoholic tinctures of *Calendula officinalis* and *Oenothera biennis* are rendered paler by acids, darker by alkalis. The same is the case with the yellow tinctures of the white flowers of *Convolvulus Sepium*, the yellow-green tinctures of *Nicotiana paniculata*, and the black parts of the flower of *Vicia Faba* (Schübler & Franck). — Yellow colouring matters soluble in water and in aqueous alcohol are also contained in *Anthemis tinctoria, Caltha palustris, Genista tinctoria, Matricaria Chamomilla, Serratula tinctoria, Solidago canadensis, Boletus hirsutus*, and many species of lichen. On a yellow resinous colouring matter from *Lichen plicatus, L. barbatus* and *L. fastigiatus,* sparingly soluble in water, easily in carbonate of soda and moderately in alcohol, see Berzelius (*Scher. Ann.* 3, 203) ; on the yellow of *Mucor septicus,* see Braconnot (*Ann. Chim.* 80, 283).

From the rinds of ripe *hips*, cold alcohol extracts a yellow and afterwards a pale scarlet resin. The former dissolves with black-green colour in oil of vitriol; it is insoluble in ammonia, but easily soluble in alcohol and in ether. The pulp of hips yields, by exhaustion with water, a soft colouring matter brown-red in the mass, saffron-yellow in thin layers, and forming with oil of vitriol a solution which is first blue, then green, then reddish, and afterwards yields black flocks on addition of water. It dissolves in ammonia with light yellow colour, in potash with brown colour, also in alcohol and in ether. The alcoholic solution forms a greenish-black precipitate with ferric hydrochlorate (Biltz, *N. Tr.* 8, 105 and 110).

The yellow of the petals of *Lychnis chalcedonica* is resinous, and dissolves with yellow colour in alcohol (John).

From the petals of *Narcissus Pseudonarcissus*, ether extracts a semifluid yellow colouring matter, which dissolves with fine yellow colour in acids and in alkalis, but is insoluble in water and in alcohol. — From the petals previously exhausted with ether, boiling alcohol slowly extracts a yellow colouring matter, brown in thick layers, which deliquesces when exposed to the air, is turned paler by acids, darker by alkalis, and is precipitated with fine yellow colour, by sugar of lead and by alum mixed with carbonate of potash (Caventou, *J. Pharm.* 2, 540; *Ann. Chim. Phys.* 4, 321).

From the fruit of *Solanum mammosum*, an orange-yellow colour is obtained by exhausting the alcoholic extract with ether. It is greasy, sparingly soluble in boiling water, soluble in oil of vitriol, cold hydrochloric acid and nitric acid, with brick-red colour, and precipitable by water. It dissolves easily in alkalis, forming deep-yellow solutions, from which it is precipitated by hydrochloric acid in siskin-green flocks; it is likewise easily soluble in alcohol and in ether (Morin, *J. Chim. méd.* 1, 88).

When the flowers of *Verbascum Thapsus*, after exhaustion with water, are digested in alcohol, the solution evaporated, and the residue freed from matters soluble in ether and in water, the colouring matter remains as a black-brown mass, yielding by trituration a siskin-green powder; it is easily soluble in alkalis and precipitable by acids. It dissolves in acetic acid, and is precipitated therefrom by water. The alcoholic solution forms a yellow precipitate with neutral acetate of lead (Morin, *J. Chim. méd.* 2, 231).

Andirin. — From the wood of *Andira anthelmintica*. The concentrated decoction of the wood is mixed with hydrate of lime, whereby it acquires a dark-green colour, filtered after 48 hours, evaporated to a syrup, and freed from a peculiar resin by alcohol. The residue, Peckolt's andirin, is yellow-brown, strongly bitter, easily soluble, with dark-red brown colour, in aqueous alkalis, and forms a black-brown precipitate with ferric hydrochlorate. It dissolves in oil of vitriol with dark brown-red colour, is not precipitated by water, dissolves sparingly in dilute sulphuric acid, also in nitric, hydrochloric, and acetic acids. It dissolves with brown colour in water, is insoluble in alcohol and in ether, but soluble in oils, both fixed and volatile (Peckolt, *N. Br. Arch.* 96, 37).

Resinous Turmeric-yellow. Curcumin. — From the root of *Curcuma longa.* 1. Lepage (*N. Br. Arch.* 97, 240) exhausts the coarsely-bruised roots twice with sulphide of carbon; the undissolved portion, after

being dried, is treated with water containing 2 p. c. hydrate of soda, and the alkaline solution is precipitated by hydrochloric acid. The washed precipitate, purified by solution in ether and evaporation, forms an orange-yellow powder, insoluble in sulphide of carbon and in benzol. — 2. The root, after exhaustion with water, is macerated in alcohol, the solution is evaporated, and the extract treated with ether, which dissolves the curcumin and leaves brown extractive matter. — Red-brown in the mass, of a bright-yellow colour when finely divided or in solution. Melts above 50°. Tasteless at first, then sharp and peppery. Does not yield ammonia by dry distillation. Very slightly soluble in cold, somewhat more in boiling water, forming a yellow solution. Easily soluble in alcohol, ether, and oils, both fixed and volatile (A. Vogel & Pelletier). — Curcumin heated with ammonia to 150° for 24 to 96 hours, forms an amide analogous to that of quercetin (p. 495). Schützenberger & Paraf. (*Muhl. Soc. Bull.* 1861, 503).

The yellow colour of curcumin is turned somewhat paler by most (dilute) acids, brown-red by alkalis, and yellowish-red by boracic acid (Müller, *A. Tr.* 16, 1, 96 : A. Vogel, *Schw.* 18, 212). The red colour is much weaker with vitrified than with unvitrified boracic acid having a stronger mineral acid still adhering to it; turmeric-powder, reddened by boracic acid, likewise assumes a dark-red colour on addition of oil of vitriol or another mineral acid; and if excess of ammonia or potash be then added, a violet colour is produced, which, however, soon gives place to a brownish-yellow (Desfosses, *Ann. Chim. Phys.* 16, 76).

The alcoholic extract of turmeric-root, left in contact with borax and hydrochloric acid, deposits a resin of a fine red colour, free from boracic acid. This resin is coloured darker by ammonia, then brownish-yellow by hydrochloric acid. It is not altered by dilute hydrochloric acid; oil of vitriol colours it black-brown, changing to brownish-yellow on addition of water. Nitric acid gives it a fine violet colour, and phosphoric acid evaporated with it to a syrup heightens the red colour; the yellow colour is in both cases restored by water (Ludwig & Streck, *N. Br. Arch.* 106, 169).

Concentrated hydrochloric and sulphuric acids likewise redden turmeric-yellow (Gmelin). Phosphoric, hydrochloric, nitric, and especially sulphuric acids colour it bright crimson, but on addition of water the yellow is precipitated in its original state; it is destroyed, however, by drenching with 4 pts. oil of vitriol, and, on the other hand, oil of vitriol diluted with 4 pts. water does not redden it at all. Vegetable acids, sulphurous, phosphorous, hydrosulphuric, and carbonic acids, do not redden the yellow; acetic acid dissolves it with yellow colour. Alcoholic tincture of turmeric is precipitated yellow or reddish by lead-, tin-, mercury-, and silver-salts, and coloured dark-brown by iron-salts. With solution of gelatin it forms an abundant yellow precipitate, which gives up only part of its colouring matter to boiling alcohol (A. Vogel & Pelletier, *J. Pharm.* 1, 291).

The *curcumin* of A. Vogel, jun. (*Repert.* 77, 274), is extracted from the root by dilute potash-ley, and separated as a yellow precipitate by acids. Or the root is freed from gummy matters by repeated boiling with water, the residue is boiled with alcohol of 80 p. c., the dark red-brown tincture is evaporated down, the curcumin, together with oil, extracted from the residue by ether, the ether evaporated, the residue redissolved in alcohol, and the solution precipitated by neutral acetate of lead. The yellowish-red precipitate is decomposed by hydrosul-

phuric acid, and the curcumin is extracted from the precipitate by ether, and obtained as an amorphous resin by evaporating the solution. It is transparent, with deep-red colour, in thin layers, cinnamon-brown in the mass, of a fine yellow colour in powder; melts at 40°, but does not sublime; consists of 69·5 p. c. carbon, 7·46 hydrogen, and 23·04 oxygen. The precipitate thrown down from the alcoholic solution by alcoholic sugar of lead, contains 43·67 to 56·32 p. c. lead-oxide.

Resinous Annatto-red. Colouring-matter of *Annatto.* — The pellicle of the seeds of *Bixa Orellana* — called *Annotte, Anatto, Annatto, Orlean,* and *Roucou* — is obtained on the large scale by mechanical treatment of the seeds with water, from which it is deposited; it contains a yellow colouring matter soluble in water, called *Orellin,* and a red colouring matter called *Bixin.*

John (*Chem. Schriften,* 2, 73) obtains the resinous colouring-matter by exhausting annatto with alcohol, evaporating the solution, treating the residue with ether, and evaporating as a deep brown-red mass, soft, glutinous, and fusible. It dissolves in oil of vitriol with an indigo-colour, changing to greenish, and then to brownish-black. Annatto prepared by triturating the seeds is likewise coloured indigo-blue by oil of vitriol (Boussingault, *Ann. Chim. Phys.* 28, 440). The colouring matter obtained as above still retains a turpentine-like body and a fatty acid. To remove the former it is dissolved in alcohol, boiled, after addition of soda-ley, till the alcohol is evaporated, shaken up with water and ether, and the ethereal layer is drawn off. By saturating the aqueous alkaline solution with carbonic acid, and filtering off the precipitate which forms after standing for some time, the fatty acid is also partially removed, and the rest of it may be got rid of by mixing the filtrate with a small quantity of acetic acid, and agitating with ether. After the ethereal layer has been removed, the addition of a larger quantity of acetic acid precipitates the colouring matter, which, after drying, solution in ether, and evaporation of the ethereal solution, is obtained as an amorphous mass, yielding a blood-red powder, and not melting at 100°. It dissolves easily in aqueous alkalis and in soap-water, and is not precipitated from the alcoholic solution by acetate of baryta, but alcoholic sugar-of-lead precipitates it with red colour. It is slightly soluble in cold alcohol and ether, dissolves abundantly in hot alcohol and in benzol, with red colour, changing to yellow on dilution (Bolley & Picard, *Dingl.* 162, 139; *Chem. Centr.* 1861, 887; *Kopp's Jahresb.* 1861, 709).

When annatto is washed with water by decantation, to remove yellow colouring matter and impurities, the residue dried and boiled with alcohol, the tincture evaporated, and the residue treated with ether, the ether takes up the bixin and leaves it behind on evaporation. Its solution in a small quantity of alcohol, when exposed to a very low temperature, still deposits foreign substances, after the removal of which, acetic acid throws down purer bixin. This, when dry, is red, amorphous, soluble in alcohol, ether, and potash-ley, and is coloured blue by oil of vitriol. Its composition agrees with the formula $C^{14}H^{13}O^2$ (Kerndt, *Dissertatio de fructibus asparagi et bixæ orellanæ.* Leipzig, 1849; *Handwörterbuch,* 57, 541).

The seed-coating of *Euonymus europæus* contains a colouring matter related to annatto (Wahlenberg).—The colouring matter of asparagus-

berries dissolves with orange-red colour, in volatile and fixed oils, and acquires an indigo-blue colour by contact with oil of vitriol. The same colouring matter occurs in *carrots*, in *woody nightshade*, and in the *gourd ;* it is identical with that of annatto. Braconnot (*N. Ann. Chim. Phys.* 20, 362). Kerndt finds in asparagus-berries a yellow colouring matter, *Chrysoïdin*, and a red, *Eoïdin* $C^{24}H^{22}O^3$, both similar to, but not identical with, that of annatto.

Taigutic acid. The yellow colouring matter of the Taigu wood of Paraguay. — It is extracted from the wood by cold alcohol, and purified by repeated treatment with alcohol and ether.

Fine yellow crystals, which slowly turn brown when exposed to light. Tasteless. Melts at 135°, without loss of weight, to a thin liquid, and solidifies in crystalline needles on cooling. Volatilises at 180° without residue, in yellow vapours which condense to needles. — Free from nitrogen.

In dry *chlorine-gas*, it deliquesces, with rise of temperature and evolution of hydrochloric acid gas, to a scarlet oil, which afterwards solidifies to a translucent wax, free from *chlorine*. — It absorbs *iodine vapour*, and turns red. With iodine- and chlorine-water it turns brown, with bromine-water, red. It dissolves in *oil of vitriol*, with orange-red colour, and water throws down from the recently prepared solution, but not from that which has been kept for some time, needles which dissolve in water more readily than taigutic acid. The same needles separate on cooling from solutions of taigutic acid in dilute hydrochloric acid or sulphuric acid prepared at the boiling heat. — Melts to a red liquid in *hydrochloric acid gas*, but less quickly than in chlorine. — By cold strong *nitric acid*, it is slowly converted into an orange-red product; hot nitric acid acts on it violently, and dissolves it with the same colour. — When distilled with *hydrate of potash*, it yields an aromatic oil.

Dissolves in 1000 pts. boiling *water ;* heated with water to 149° in a sealed tube, it dissolves in large quantity and crystallises out on cooling.

Dissolves in aqueous *alkalis*, with red colour, perceptible even in very dilute solutions. The solution does not absorb oxygen. — The acid decomposes alkaline carbonates. It forms insoluble salts with baryta, strontia, and oxide of lead, and is separated from its salts by mineral acids.

Ammonia-salt. — The solution of the acid in aqueous ammonia yields, by evaporation over lime and sal-ammoniac, prisms of a fine blood-red colour. The salt gives off ammonia when exposed to the air.

Potash-salt. — Long orange-red prisms, not deliquescent, but easily soluble in water; soluble also in alcohol, and to a smaller amount in ether.

Lead-salt. — Obtained by double decomposition. Scarlet precipitate, becoming orange-red and crystalline in contact with water. Nearly insoluble in water, easily soluble in alcohol, and separates in needles on evaporation.

Silver-salt. — Obtained from the ammonia-salt and nitrate of silver, as a cinnabar-coloured precipitate which decomposes on exposure to light. Soluble in ammonia and in alcohol, nearly insoluble in ether.

The acid dissolves in *sulphide of carbon*, in *wood-spirit*, in 86·2 pts. *alcohol* of 84° ; in 19·2 pts. *ether ;* 15·8 *acetone ;* 41·8 *benzol*, also in

naphtha, less easily in *glycerin, oil of turpentine,* and *sugar-water* (Arnaudon, *Compt. rend.* 46, 1154).

B. *Blue and Red Colouring Matters.*

1. Blue of Flowers.

Anthocyan (Marquart) ; Cyanin (Frémy & Cloez). According to Filhol, it is identical with *œnolin* (xvi, 478).

This substance constitutes the colouring matter of blue flowers ; in combination with acids, that of red flowers ; and with weak acids, such as carbonic acid, that of violet flowers (Marquart). Orange-yellow flowers contain reddened anthocyan and anthoxanthin ; brown flowers contain anthocyan and chlorophyll (Marquart). Scarlet flowers contain cyanin with xanthin, and xanthein (p. 513) (Fremy & Cloez). Black is mostly produced by anthocyan (or by chlorophyll) ; the black of *Vicia Faba* differs from other colouring matters by its insolubility in water, alcohol, and ether. The green which the blue flowers of *Gentiana acaulis* exhibit on their edges, is produced by yellow cells lying beneath the superficial blue cells (Marquart). — Many white flowers also contain anthocyan, in consequence of which they are turned green by alkalis, and, like those of the white fox-glove, are reddened by acids (Schubler & Franck).

Anthocyan is extracted by cold alcohol of 85 p. c. from fresh flowers freed from calyx, stamens and ovaries ; in a few cases only, as with *Scilla sibirica,* is it necessary to use weaker alcohol of 40 p. c. — The tincture of blue flowers is mostly colourless or reddish, seldom blue, as with *Dracocephalum altaïcum,* or green, as with *Gentiana acaulis ;* that of violet flowers is colourless or reddish ; that of red flowers, colourless, yellowish, reddish, or even quite red. The colourless tinctures are turned red by acids, blue or green by alkalis.

When the alcoholic tinctures are evaporated at a very gentle heat, there remains a mixture of anthocyan and resinous matter, from which water takes up the anthocyan, leaving it, on evaporation, as a blue, or if it contains acid, violet or red mass, very hygroscopic, permanent when dry, but decomposing very quickly in solution. It is decolorised by chlorine-water, coloured red by acids, green by alkalis ; ferric salts deepen the colour of the solution, and precipitate it ; solution of gelatin and tincture of galls produce no precipitate. It dissolves in water and in alcohol of 50 to 60 p. c., but is insoluble in absolute alcohol, ether, and oils both fixed and volatile. The aqueous solution is for the most part blue, but often loses its colour in a few seconds, even in open vessels and in the dark, as in the case of *Vinca minor, Lolium perenne,* and *Dracocephalum altaïcum.* The decolorised solution becomes violet-coloured on exposure to the air ; it then reddens litmus, and leaves the anthocyan on evaporation, as a substance of a dark indigo-blue colour. — The green colour produced by alkalis passes after 12—24 hours into yellow and brown, the colouring matter being at the same time decomposed. — Neutral acetate of lead colours the solution of anthocyan green ; basic acetate of lead colours it yellow-green ; boracic acid does not act upon it in most cases, but colours the

solutions of anthocyan from *Vinca minor*, *Dracocephalum*, and *Primula Auricula*, violet, like carbonic acid; in other cases it changes the colour to greenish blue, like the alkalis. — Alum mostly deepens the blue colour, but sometimes (as with *Vinca, Linum*) acts like a weak acid, sometimes (as with *Gentiana acaulis*) changes the blue colour to green. Protochloride of tin changes the colour to violet, like weak acids. Dry anthocyan is turned yellow or brown by oil of vitriol, the colour changing to a fine purple-red on dilution with water. — Anthocyan reddened by acids is completely decolorised by zinc, but quickly turns red again on exposure to the air (Marquart).

The *violet colouring matter of flowers* behaves like anthocyan, but is more soluble in strong alcohol, so that alcohol of 86 p. c. decolorises all violet flowers. In *Iris pumila* it passes, on repeated evaporation and solution, into blue, perhaps from loss of a volatile acid. The violet flowers of *Nonea rosea* immersed in alcohol, gradually become dark blue, and form a greenish yellow acid tincture, which is resolved by evaporation into anthocyan and a sulphur-yellow resin. Violet flowers which have turned blue do not give up their colouring matter to alcohol till carbonic acid is passed through the liquid. The aqueous solution of the violet colouring matter has a deeper colour than that of the blue, and is coloured blue by cautious addition of alkalis; a very small quantity of a lead-salt turns it blue; a larger quantity forms a green precipitate. Boracic acid acts on the violet for the most part like an alkali, so likewise does alum; protochloride of tin acts like a weak acid (Marquart).

The *colouring matter of all red flowers* (see below) consists of anthocyan reddened by acids, but more soluble in alcohol. Its aqueous solution is seldom decolorised, and then but partially. By repeated evaporation and solution, it leaves a red-violet or blue residue, sparingly soluble in water (Marquart's *Deposited colouring matter*), which recovers its former properties when treated with a small quantity of acid. The aqueous solution of red anthocyan always reddens litmus; the alcoholic tincture of red or blue flowers, which is usually colourless or yellowish, does not redden litmus, excepting when the resin has been separated by evaporating off the alcohol. If the alcoholic solution of this resin is again added, the colour and acid reaction disappear. — If the tincture of red flowers has a red colour, like that of *Cactus speciossimus*, *Papaver bracteatum*, &c., it may be decolorised by addition of resin of flowers (p. 515).

Red flowers yield, with water, solutions exhibiting various shades of red, which may also be obtained by mixing anthocyan with acids. Acids heighten the colours of the aqueous solutions; a very small quantity of alkali changes the red to blue, a larger quantity to green, easily passing into olive-green and brown. Lead-salts added in small quantity produce a blue, in larger quantity a green precipitate. Boracic acid acts always like the alkalis; alum sometimes like a weak acid (Marquart).

The black colour at the base of the petals of *Tulipa Oculus solis* is produced by dark indigo-coloured anthocyan, and in like manner the dark spots in *Gazania rigens* and *Arum Dracunculus*. The black colour of the spots of *Pelargonium tricolor*, *Orchis maculata* and *O. mascula* is produced by superposed layers of violet cells. In some cases the black colouring is produced by chlorophyll (Marquart).

According to Elsner also (*Schw.* 64, 165) the red of purple, rose,

and vermilion-red flowers is produced by one and the same colouring matter, which, however, forms precipitates of different colours with certain metallic salts. If the fresh petals be freed from their waxy coating by ether, and the residue exhausted with alcohol of sp. gr. 0·835, the flowers become decolorised. The tincture obtained from dark flowers is lighter than the flowers themselves. That from pale flowers is greenish, and leaves the colouring matter on evaporation as a dark, shining film, which may be further purified by precipitating its aqueous solution with basic acetate of lead, and decomposing the green precipitate under alcohol with hydrosulphuric acid. — This red dissolves easily in water, and in aqueous alcohol, not in ether or in oils. It is coloured deep red by hydrochloric acid, light green afterwards, yellow by alkalis, and green by alkaline carbonates. According to Elsner, it is produced from chlorophyll (Elsner, *Schw.* 64, 165).

The red colouring matter of roses, dahlias, or pæonies, which may be obtained in the same way as cyanin, consists of cyanin reddened by acids (Frémy and Cloez).

Rose-red and blue flowers contain two colouring matters, one of which is colourless in acid, yellow in alkaline liquids (therefore xanthein), while the second is turned red by acids, and blue by alkalis, and the mixture of the two is turned green by alkalis (Filhol).

According to Stein (*J. pr. Chem.* 89, 491), most red flowers contain *paracarthamin* (a red substance produced by the action of sodium-amalgam and hydrochloric acid on meln, meletin, and morin, and having the composition $C^{20}H^{12}O^{10}$?); in some, however, the colouring matter appears to be somewhat different, inasmuch as it is coloured blue by acetate of alumina, whereas paracarthamin is coloured green. Stein is also of opinion that paracarthamin may exist in blue flowers combined with bases more or less powerful, as it may be made to pass by the action of alkalis through all shades of colour from red to blue.

Perfectly dry blue flowers (violets, irises, campanulas, and many others) do not lose their colour when kept for a year in dry air or oxygen gas, either in the dark or in sunlight; but in contact with moist air or oxygen gas, they are quickly decolorised if exposed to light, more slowly in the dark; even in moist hydrogen or carbonic acid, decoloration takes place in two or three weeks. In calcareous spring-water the flowers turn green, as when treated with alkaline bicarbonates; to pure water they give up their colouring matter, with violet, or if the flowers contain an acid, with red colour. If the liquid contains only a small quantity of colouring matter, it loses its colour completely when heated; if it contains more, it turns red. — Perfectly dry blue flowers do not alter at 100°, or at temperatures a little above; but when moist they lose their colour at 40° or 50°. — A very small quantity of alkali (bicarbonate of soda or morphine answers best) colours the infusion darker blue, a larger quantity greenish blue, then green, and finally yellow. — Acids colour the blue red, and the solution, if not heated, remains for a long time unaltered; but if heated, assumes a brown-yellow colour, and is reddened, and afterwards decolorised by sulphurous acid. Volatile oils shaken up with the blue infusion turn it red and then decolorise it. — Strong alcohol does not extract any blue, but only a rose-red from reddish-blue flowers (Hünefeld, *J. pr. Chem.* 2, 217).

Blue and red flowers or fruits are bleached by sulphurous acid, either in the dark or when exposed to light, even without access of

oxygen. All bodies which convert sulphurous into sulphuric acid, such as ozone, ozoniferous liquids, chlorine, bromine, iodine and peroxide of hydrogen, restore the colour, at least for a while; even hydrosulphuric acid produces this effect, by decomposing the sulphurous acid; also hot aqueous vapour and dilute mineral acids, by driving it out. — Yellowish red flowers turn yellow in sulphurous acid, but recover their original colour when the sulphurous acid is decomposed or removed. As their red colour is bleached by sulphurous acid, while the yellow is not, that acid may serve to detect the yellow colouring matter when present, even in the red parts of plants (Schonbein, *J. pr. Chem.* 53, 321, and 54, 76).

Violets, irises, and pæonies colour alcohol but slightly, losing their own colour, however, at the same time. The extract prepared with boiling water, has also but little colour, but both this and the alcoholic extract are coloured bright red by acids. It is decolorised by the infusion of white flowers more easily than by water (Filhol).

Many flowers are turned green by alkalis, others blue. The infusion of *Pelargonium zonale* (also of *P. inquinans* and of red pæonies) remains blue for several days; that of violets becomes green, then quickly yellow. The slightly coloured tincture of red pæonies is turned green by ammonia, but blue if previously mixed with an acid (Filhol, *Compt. rend.* 39, 194; 50, 1182).

The infusion of the blue flowers of the larkspur is not decolorised by aqueous hydrosulphuric acid in a fortnight (A. Vogel, *J. pr. Chem.* 16, 314).

The blue juice of violets turns reddish in closed vessels kept in the dark, but recovers its blue colour on exposure to the air (Gehlen, *Schw. J.* 10, 119). It is reddened by most strong acids, but sulphurous acid colours the red juice blue again (Planche, *Ann. Chim.* 60, 253). With the blue juice it forms a colourless compound, which is turned red by the stronger mineral acids, and green by alkalis (Grotthuss, *N. Gehl.* 7, 699). Boracic acid, and certain metallic salts, turn the blue of violets to green (Murray, *Schw.* 33, 487). Alkalis change the blue to green, then quickly to yellow and brown, with precipitation and decomposition, oxygen being at the same time absorbed (Chevreul). Peroxide of hydrogen containing baryta, turns violet-juice green, and decolorises it completely in 24 hours (Chevreul, *Compt. rend.* 55, 737). The blue dissolves easily in alcohol with pale red colour (Gehlen).

The flowers of *Mirabilis Jalappa* colour water slightly red; alcohol, which decolorises them, strongly red. Ether extracts from the fresh flowers, only a yellow colouring matter, while the red is deposited in combination with the water of the flowers. This red precipitate is purified by washing with ether, solution in alcohol, and precipitation with ether; it dissolves readily in water, is quickly decomposed by chlorine, coloured brighter red by acids, but quickly brought back to yellow by mineral acids or by alkalis (Roux, *J. Pharm.* 11, 510; *N. Tr.* 12, 2, 100).

Red verbenas and *Anemone hortensis* colour alcohol violet-red, and ammonia imparts to the tincture a wine colour, inclining to green. Dry hydrate of alumina immersed in the tincture, acquires a yellowish colour, and the supernatant liquid acquires a fine red colour when mixed with acids, pure blue with bases (Filhol).

The colouring matters of the following flowers agree with antho

cyan, in so far as they are turned red by acids, green or yellow-green (sometimes blue at first) by alkalis, and yield yellow-green precipitates with neutral acetate of lead. This is the case with the red colour of *Althæa rosea, Amaryllis speciosa*, artichokes, (see also under *Chlorophyll*) asters, the *Bellis perennis* (Schübler & Franck); *Borago officinalis* (Lampadnus, Schübler & Franck); *Campanula Trachelium, Cheiranthus incanus, Cichorium Intybus, Dahlia pinnata* which is turned green by the smallest quantity of alkali (Payen); *Delphinium Ajacis, Digitalis purpurea, Gentiana Pneumonanthe*, pæonics, pomegranate-flowers (Schübler & Franck), blue hortensias [that from red hortensias is turned blue by dilute alkalis (Schübler & Lachenmeyer, *J. pr. Chem.* 1, 46)], *Hemerocallis carulea*, blue hyacinths, lavender, *Linum perenne, Lythrum Salicaria* (Schübler & Franck), *Malva sylvestris*, which is very sensitive to alkalis (Chevallier, *J. Chim. méd.* 10, 407; Payen & Chevallier, *J. Pharm.* 8, 483); pinks, roses, *Veratrum nigrum* and violets (Schübler & Franck).

In the following cases, the colouring matter appears to differ from anthocyan :

The flowers of the *Aloe* contain a red which dissolves slightly in water and ether, easily in alcohol, is not altered by acids or bases, but forms fine red lakes (Filhol).

The deep orange-red flowers of *Cacalia coccinea* contain a resinous colouring matter, soluble in ether, insoluble in water and in alcohol; also a second extractive colouring matter soluble in water and alcohol, which in thin layers has a golden-yellow, in thicker layers a brownish-yellow colour, is coloured lighter by acids, darker by alkalis, and yields fine yellow precipitates with neutral and basic acetate of lead (Elsner, *Schw.* 65, 169).

The red sepals of *Calycanthus floridus* are green inside; the upper very thin layer is dark red. On drenching them with ether, a dark crimson layer of liquid settles down below the colourless ether, and when abandoned to spontaneous evaporation, leaves a green residue, changing to a splendid red when treated with acids. Alcohol likewise extracts the calycanthus red, leaving the sepals of a green colour; the tincture soon assumes a wine-yellow colour, is turned red again by acids, becomes greenish-violet for a while when neutralised, and colourless after a few hours (J. Muller, *N. Br. Arch.* 40, 146).

The flowers of *Cactus speciosus* contain about 30 p. c. colouring matter, which they do not yield either to ether or to absolute alcohol. Spirit of 60 or 70 p. c. extracts from them a carmine colour, and the residue, treated with ether-alcohol, still yields from 5 to 10 p. c. of a scarlet dye, both soluble in water (Voget, *Ann. Pharm.* 5, 205).

The red colouring matter of *Cactus speciosissimus, C. Phyllanthus* and other species, may be extracted by water containing acetic or hydrochloric acid. The beautifully bluish-red extract is not bleached by sulphurous acid, and so far behaves differently from the blue or red of other flowers. It is bleached and completely destroyed (like indigo-blue) when exposed to light in a mixture of sulphurous acid and oxygen (Schönbein, *J. pr. Chem.* 53, 321). Buchner (*Repert.* 56, 156) found the colouring matter of the flowers of *Cactus flagelliformis* and *C. Phyllanthus* easily soluble in water and in alcohol, and regarded it as a mixture of anthocyan and anthoxanthin.

The ripe, pale, purple-red fruits of *Cactus Opuntia* yield a large quantity of a fine red juice, which does not yield any colouring matter to ether or absolute alcohol when shaken up therewith. On boiling

the juice with alcohol of 80 p. c. the alcohol immediately acquires a dark red colour, but does not take up all the colouring matter; and the tincture, if decanted and distilled, turns yellowish after boiling for some time, the red colour not being restored by acids. The aqueous solution of the red turns brown when evaporated. The concentrated aqueous solution of the red juice is coloured violet by protochloride of tin, but does not form any precipitate; neither is it precipitated by solution of alum. The colour of the fruits is therefore very unstable and different from carmine (Wittstein, *Repert.* 72, 1).

Red resinous colouring matter of Hypericum. Hypericum-red. — When the flowers, freed from their calices and dried, are exhausted with absolute alcohol and the tincture is evaporated, a soft residue is left containing the red, together with volatile oil. — If the flowers are exhausted with water, then with dilute alcohol, well dried after exhaustion, and the colouring matter extracted from them by ether, it remains on evaporation as a blood-red resin, having an odour of camomile. It melts below 100° and does not yield ammonia by dry distillation. It is insoluble in water and in dilute acids. By aqueous ammonia, potash and soda, it is coloured green and dissolved; the saturated solution is red by reflected light, but exhibits after dilution a green colour by transmitted light. The ammoniacal solution leaves on evaporation a neutral blood-red resin having the odour of hypericum, soluble with yellow colour in water, and giving off ammonia when treated with potash. — The red combines also with the alkaline earths, earths proper, and heavy metallic oxides; its alcoholic solution precipitates the alcoholic solution of chloride of calcium, also neutral acetate of lead, and ferric hydrochlorate. — It dissolves in alcohol, more readily in ether, with wine-red to blood-red colour, also in volatile oils and in warm fixed oils (Buchner, *Repert.* 34, 233). According to Marquart, the colouring matter of the fresh flowers is a mixture of anthocyan and anthoxanthin, separable by exhausting with alcohol and treating the residue with water.

The colouring matter of the flowers of *Lobelia fulgens* and *L. splendens* is carmine-red, and for the most part soluble in water, but contains also a small quantity of red resinous colouring matter (John, *Chem. Schriften.* 4, 115).

The blue colouring matter of blackish tulip-pollen is soluble in water and in alcohol; its solution is reddened by acids and by nitrate of silver, forms emerald-green precipitates with lime-water and neutral acetate of lead, and a violet blue precipitate with nitrate of silver (John, *Schw.* 12, 214).

Rheadic and Papaveric acids form, according to Leo Meier, the red colouring matter of the flower of the common red poppy, *Papaver Rheas.* — According to Smithson (*Schw.* 32, 421), the red petals of this plant are turned green by potash, but are not altered by ammonia or carbonate of soda; those of *Papaver dubium*, are turned blue by alkalis (Wallenberg). — Filhol also finds (*Compt. rend.* 39, 194) that the colouring matter of the red poppy is different from anthocyan.

a. *Rheadic acid* (Rhoeadinsäure). — The aqueous extract of the flowers prepared at the boiling heat is mixed with solution of neutral acetate of lead, or boiled with carbonate of lead, whereby rheadate of lead is precipitated; the precipitate is freed from adhering papaveric acid by

washing, five or six times repeated decomposition, and reprecipitation; and the rheadic acid is separated from the oxide of lead by boiling alcoholic sulphuric acid, a small portion of the lead-salt however still remaining undecomposed. — On evaporating the alcoholic filtrate, the acid remains behind. If hydrosulphuric acid is used to decompose the lead-precipitate, the acid obtained has a brick-red colour, indicating decomposition.

Shining amorphous mass having a fine dark red colour. Tastes purely sour and reddens litmus. — Does not yield ammonia by dry distillation. The aqueous acid is coloured yellowish by chlorine or by hot nitric acid. Hot oil of vitriol carbonises the dry acid; evaporation with excess of potash forms a dark brown mass.

The acid dissolves readily in water, colouring it deep red; the solution exposed to air and sunshine in a loosely covered vessel remains unaltered for three weeks. — The aqueous solution is coloured violet by lime and baryta-water, without precipitation; also by ammonia and carbonate of potash, from which it expels the carbonic acid.

The salts of rheadic acid are blue or bluish-grey and amorphous. They are obtained by neutralising the acid with the base, or by double decomposition, and are all soluble in water, excepting those of the heavy metals. Sulphuric acid separates the rheadic acid from them in its original state.

b. *Papaveric acid (Klatschrosensäure).* When the hot infusion of red poppies is boiled with carbonate of lead, filtered from rheadate of lead, and the violet filtrate, free from lead, is evaporated, there remains a mixture of papaveric acid and lime-salts, from which the lime may be separated as sulphate by careful addition of sulphuric acid. — The solution is evaporated; the residue boiled with alcohol of 60 p. c.; and the liquid filtered from gypsum and gum, is evaporated, whereupon the acid remains as a fine red amorphous mass, still retaining a small quantity of gypsum. — Inodorous; has a slight acid taste and reaction. Does not yield ammonia by dry distillation. The acid is deliquescent; its aqueous solution has a rose-red colour. By prolonged boiling with dilute sulphuric acid, it yields a dark-coloured deposit. — The alkalis, baryta-water and lime-water colour it violet, but do not precipitate it; neither is it precipitated by neutral acetate of lead, ferric hydrochlorate, acetate of copper, or nitrate of silver.

It is insoluble in ether and in absolute alcohol, easily soluble in boiling alcohol of 60 to 80 p. c. The solution does not form a precipitate, either with tannin or with gelatin (See Meier, *Repert.* 91, 346).

2. Blue and Red Colouring Matters of Berries.

The red of berries does not always consist of anthocyan reddened by acids, being red in some cases, even when all but neutral. In most cases the juices or tinctures are coloured bright red by acids, blue by alkaline carbonates, (blue and then) green by caustic alkalis, and precipitated blue by neutral acetate of lead. Such is the case with blackberries John, *Chem. Schw.* 4,

177; Schübler & Franck), raspberries (Schübler & Franck), mulberries (Smithson, *Phil. Trans.* 1818, 1), the fruit of *Prunus Malaheb* (Payen & Chevallier, *J. Pharm.* 8, 489), the berries of *Actea spicata* (Wahlenberg), bilberries, lilac berries (A. Vogel, *Schw.* 20, 416; Schübler & Frank), the berries of *Sambucus canadensis* (Cozzens), *Sambucus nigra* (Chevallier, *J. Pharm.* 6, 177), *Atropa Belladonna* (Melandri, *Ann. Chim.* 65, 223), *Rhamnus Frangula* and *Rh. Cathartica* (Smithson; Schubler & Frank). The violet colouring matter of the berries of *Sambucus Ebulus* appears to be identical with anthocyan (Enz, *Pharm. Viertelj.* 1, 509).

The juice of *black cherries* and of *currants* is likewise turned green by caustic alkalis, blue by alkaline carbonates (Smithson). According to Berzelius, it is red, even when approaching as near as possible to neutrality. — When the juice of cherries or black currants is digested with finely pounded chalk to precipitate citric and malic acids, then with a small quantity of lime to remove neutral malate of lime,— the filtrate mixed with a small quantity of neutral acetate of lead— the precipitate, perhaps still retaining malic acid, removed,—and the filtrate precipitated with a larger quantity of neutral acetate of lead,—the resulting green precipitate contains all the dissolved colouring matter. It is washed with water, with the least possible access of air, and decomposed by hydrosulphuric acid; the filtrate is evaporated in vacuo over oil of vitriol; the residue dissolved in absolute alcohol, which leaves behind the colouring matter altered by exposure to the air, together with pectous substances; and the alcoholic solution is evaporated finally in a vacuum. The juice may also be first treated with neutral acetate of lead to precipitate citric and malic acid, and the filtrate with the basic acetate, to throw down the colouring matter.

Translucent shining mass of a fine red colour. — By evaporation of its aqueous solution, it is partly converted into a red-brown colouring matter less soluble in water and alcohol, and dissolving with dark brown colour in alkalis. The green neutral solutions of the unaltered colouring matter in alkalis pass, on exposure to the air, into the brown compound of the altered colouring matter.

Soluble in all proportions in water. A small quantity of milk of lime, not sufficient for complete precipitation, throws down a portion of the colouring matter, with greyish green colour, while the rest remains dissolved, with red, but with somewhat altered colour. The green precipitate formed by basic acetate of lead remains unaltered for years, after washing and drying.

Soluble in all proportions in alcohol; insoluble in ether (Berzelius, *Ann. Pharm.* 21, 262; *Pogg.* 42, 431).

The red colouring matter of *Strawberries* is obtained from the juice. The pectin is precipitated by alcohol, malic acid by cautious addition of neutral acetate of lead, then the colouring matter by a larger quantity of that salt. This colouring matter turns green in contact with potash, and yields, with an alcoholic solution of neutral acetate of lead, first a blue, then a red precipitate (Schweizer). According to Wittstein, it exhibits the reactions of cissotannic acid (xv, 516). It may be obtained in a somewhat altered state by first exhausting the seeds with ether, and afterwards treating them with alcohol, but it is then insoluble in water (Schweizer, *Schweiz. Apoth. Mitth.* 1851, 169; *Pharm.*

Viertelj. 2, 425).   On the juice of the berries of *Phytolacca decandra*. See Braconnot (*Ann. Chim.* 62, 81).

The ripe fruits of *Arbutus Unedo* contain a colouring matter, which is coloured violet by alkalis, and red by acids (Filhol, *Compt. rend.* 50, 1185).

The colouring matter of *red* or *black grape-skins* is the substance described in vol. xiv, p. 478, under the name of *Oenolin*. See also Bizio (*Brugn. Giorn.* 17, 473), Nees v. Esenbeck (*Br. Arch.* 20, 193).

Colouring matter of the berries of Ligustrum vulgare. Ligulin. (Nicklès). — Reinsch exhausts the crushed berries with alcohol; evaporates the tincture; frees the extract from oil, wax, and odoriferous substances by means of ether; and dissolves the residual colouring matter in alcohol. The splendid dark red tincture becomes turbed on addition of ether, and deposits the colouring matter in the course of 3 or 4 days, as a red-brown mass of interlaced crystals. It dissolves in water, with blood-red colour, soon changing to brown-red (Reinsch, *Jahrb. pr. Pharm.* 16, 389). — Nicklès precipitates the filtered juice of the berries with neutral acetate of lead; decomposes the washed precipitate with hydrosulphuric acid; evaporates the solution; washes the residue with ether; precipitates it again from the alcoholic solution by neutral acetate of lead; and decomposes the lead-precipitate as above. According to Reinsch, however, the colouring matter thus obtained is impure and not perfectly soluble in water. — Ligulin is free from nitrogen; it chars when heated, but if the carbonisation is incomplete, the uncharred portion suffers no alteration. It dissolves in water, with crimson colour, and is not altered by 48 hours' boiling with water. It is not altered by six weeks' contact with sulphurous acid, nor decomposed by cold concentrated acids. — Ammonia quickly changes it into a yellow substance. Bicarbonate of lime colours the solution blue; alkalis and alkaline carbonates turn it green, and the mixture, when left to itself, takes up oxygen and decomposes. Chloride of calcium and nitrate of lime colour ligulin blue; acetate of alumina gives it a fine blue-violet colour, and on boiling throws down a blue-lake, insoluble in acetic acid, but dissolving with red colour in tartaric, citric, and mineral acids. The blue lead-salt contains from 21·5 to 23 p. c. carbon, and 1·89 to 2·58 hydrogen. Ligulin dissolves in alcohol, but not in ether. It is not precipitated by gelatin. Berries gathered in the autumn contain it in the insoluble state (Nicklès, *N. J. Pharm.* 35, 328).

The bruised, pressed, and washed berries of the *yew-tree* (*Taxus baccata*), give up to ether a carmine-coloured substance, soluble in alcohol, insoluble in water (Chevallier & Lassaigne, *J. Pharm.* 4, 558).

The name *Cacao-red* is given by Tuchen (*Ueber die organ. Bestandtheile des Cacao*, Gott. 1857; abstr. *Kopp's Jahresb.* 1857, 531) to a red colouring matter, precipitable by neutral acetate of lead from the aqueous decoction of cacao, and separable from the lead precipitate by hydrosulphuric acid. It is soluble in water and in alcohol, colours iron-salts green, and is converted into a tannic acid by oxidation. — The colouring matter of cacao-beans does not exist in the fresh beans, but is formed in them at a later period; it is extracted from the comminuted beans by acetic acid, together with a small quantity of albumin, which may be separated by repeated addition of

alcohol, and evaporation of the acetic acid. In the beans, especially in the so-called "rotted beans," the colouring matter is combined with albumin, and, in fact, a compound of this nature may be obtained, as a bulky brown precipitate, by repeatedly exhausting the beans with dilute soda-ley, and precipitating the filtrate with hydrochloric acid. The neutral violet-coloured extract of Bahia beans is coloured darker, and with a greenish tint by alkalis; red by acids; forms copious slightly coloured precipitates with a solution of gelatin containing alum, and with albumin, black with ferric salts, coloured precipitates with most other metallic salts, the supernatant liquid remaining coloured at the same time. Neutral acetate of lead precipitates the colouring matter completely. When separated from this precipitate, it is free from nitrogen, and easily decomposible (A. Mitscherlich, *Der Cacao und die Chocolade*, Berlin, 1859; abstr. *Kopp's Jahresb.* 1853, 593).

Certain *roots* contain blue or red colouring matters, which appear to be identical with the blue of flowers.

The red colouring matter of beet (*Beta vulgaris*) is very unstable. The infusion obtained by macerating the roots dried below 50° in cold water, yields, with neutral acetate of lead, a red lake, which must be well boiled with water, drenched with alcohol of 70 p. c., and heated to 60° with aqueous oxalic acid. The filtrate, which has a fine red colour, leaves, when evaporated below 50°, a red residue, which may be freed from altered yellow colouring matter (Meier's *xanthobetic acid*) by repeated treatment with absolute alcohol, whilst the red colouring matter (Meier's *erythrobetic acid*) remains in solution. The latter may be obtained in the crystalline form by slow evaporation of its solution. It may be re-solved in various ways into a brown and a yellow colouring matter (xanthobetic acid), dissolves very readily in water, but is insoluble in ether and in absolute alcohol. The lead-compound is grey or brown when dry, but when decomposed in the moist state by hydrosulphuric acid, it yields a colourless filtrate. — Xanthobetic acid is obtained in like manner from red beet which has been dried at a strong heat, and thereby turned brown. It is of fine reddish-yellow colour, lustrous, amorphous, easily soluble in water and in absolute alcohol, sparingly soluble in ether (Leo Meier, *Repert.* 95, 157).

The juice of the red beet is decolorised by hydrochloric acid and zinc, or by hydrosulphate of ammonia, and in neither case does the colour reappear on exposure to the air (Kuhlmann, *Ann. Pharm.* 9, 286).

The red colouring matter of *mangold wurzel* dissolves in lime-water, forming a yellowish liquid, which is reddened again by acids, even by carbonic acid; the red juice forms a red precipitate with neutral acetate of lead (Vogel). — The colouring matter is not immediately altered by dilute acids; alkalis colour it yellow. It dissolves easily in spirit of 25° B., but is insoluble in spirit of 40° (Payen, *J. Chim méd.* 1, 387).

The red skin of the root of *Raphanus sativus* turns blue when peeled off with an iron knife. It yields by pressure a blue juice, which is turned red by acids, and green by alkalis. The skin of the root of *Raphanus vulgaris* behaves with acids and alkalis in a similar manner (Descharmes, *J. Phys.* 96, 136). — To this place belongs also the colouring matter of purple potatoes (Reinsch, *Jahrb. pr. Pharm.* 14, 100), and of batatas (Payen & O. Henry).

ADDENDA.

Reactions of Narcotine. (A. Husemann, *Ann. Pharm.* 128, 305; *Rép. Chim. pure*, 1863, p. 284). — Narcotine added to cold *sulphuric acid*, colours it bluish violet or yellow, which, if the liquid be gently heated, changes to orange-red, then to violet-blue at the edge of the dish, and lastly to violet-red. This reaction is very distinct, if the sulphuric acid contains 1 pt. in 2,000 of narcotine; and even if it contains only 1 pt. in 40,000, a slight carmine colour is still perceptible, passing into violet-red.

A solution of narcotine in cold sulphuric acid becomes reddish-yellow on addition of *nitric acid*. With *hypochlorite of soda*, the same colour is produced, but preceded by a carmine tint. If the solution has been heated, both reagents immediately produce a light yellow colour, becoming slightly reddish after a while.

A solution of narcotine in sulphuric acid previously heated, acquires, on addition of *sesquichloride of iron*, a dark red colour, changing to cherry-red, which lasts for 24 hours (compare *Reactions of Morphine*, p 534).

Hydride of Tridecatyl.

$$C^{26}H^{28} = C^{26}H^{27}, H.$$
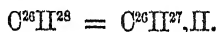
PELOUZE AND CAHOURS. *Ann. Pharm.* 129, 87.

Hydride of Cocinyl. Occurs, together with several of its homologues in the petroleum or earth-oil now imported in large quantities from North America. This oil consists mainly of the hydrides of the alcohol-radicals $C^{2n}H^{2n+2}$, homologous with marsh-gas, and by submitting it to fractional distillation, purifying the distillates by successive treatment with sulphuric acid and carbonate of soda, desiccation with anhydrous chloride of calcium, distillation over sodium, and final rectification, Pelouze and Cahours have separated twelve of these hydrides, from hydride of tetryl (butyl) $C^{8}H^{10}$, boiling at a few degrees above 0°, to hydride of pentadecatyl $C^{30}H^{32}$, boiling between 255° and 260°. All the alcoholic hydrides included within these limits are liquids of more or less agreeable odour, burning with a slightly smoky flame, and regularly increasing in specific gravity, vapour-density, and boiling point, as their molecular weights increase. They are little, if at all attacked by strong sulphuric acid, fuming nitric

acid, or bromine, but chlorine converts them all into the corresponding alcoholic chlorides $C^{2n}H^{2n+1}Cl$. — The earth-oil also yields a quantity of liquid boiling above 300°, and doubtless containing higher terms of the same series. Moreover in boring for it, large quantities of gas escape, exhibiting the characters of marsh-gas : hence it is probable that in the great geological changes which have given rise to the separation of this liquid, the whole series of alcoholic hydrides has been formed, from marsh-gas up to the highest paraffins (Pelouze & Cahours, *Ann. Pharm.* 124, 289 ; 127, 190.)

Hydride of Tridecatyl boils between 216° and 218°. It is a transparent and colourless liquid, having an odour somewhat like that of turpentine. Sp. gr. = 0·792 at 20°. Vapour-density = 6·569.

			Pelouze & Cahours.			Vol.	Density.
26 C .	 156	..	84·78 .	85 04	C-vapour 26	....	10 8160
28 H	.. 28	...	15 22 .	15 37	H-gas 28		1·9404
$C^{26}H^{28}$	 184	....	100 00	100·41	Vapour of $C^{26}H^{28}$.... 2	..	12 7564
					1	....	6 3782

Hydride of tridecatyl is not attacked by *bromine, fuming nitric,* or *strong sulphuric acid;* but a mixture of these acids attacks it at the boiling heat, and if the action be continued for some time, a small quantity of a crystallisable product is formed, a yellowish oil somewhat heavier than water separates out, and the nitrous gas evolved is mixed with the vapour of some acids having the odour of the volatile acids of the acetic series. — Chlorine converts it into chloride of tridecatyl $C^{26}H^{27}Cl$, boiling between 258° and 262°.

Page 209.

Hydride of Tetradecatyl.

$$C^{28}H^{30} = C^{28}H^{29},H.$$
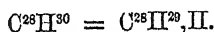
Pelouze & Cahours. *Ann. Pharm.* 129, 87.

Hydride of Myristyl. Obtained from American petroleum, as already described (p. 532). Transparent, colourless liquid, having an odour like that of hydride of tridecatyl. Boils between 236° and 240°. Vapour-density, 7·019.

			Pelouze & Cahours.			Vol.	Density.
28 C	 168	....	84·85	84 67	C-vapour 28	....	11·6480
30 H	 30	.. ..	15·15	15 25	H-gas 30	....	2 0790
$C^{28}H^{30}$	 198	....	100 00	99·92	Vap. of 6 $^{28}H^{30}$ 2	....	13·7270
					1	....	6 8635

Behaves with *bromine, nitric acid, sulphuric acid,* and a mixture of the two, just like hydride of tridecatyl. — *Chlorine* converts it into chloride of tetradecatyl, $C^{28}H^{29}Cl$, boiling at about 280°.

Page 286.

Hydride of Pentadecatyl.

$$C^{30}H^{32} = C^{30}H^{31},H.$$
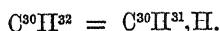
PELOUZE & CAHOURS. *Ann. Pharm.* 129, 89.

Obtained from American petroleum, as described at page 532. Transparent, colourless liquid, having an odour similar to that of hydride of cocinyl. Boils between 255° and 260°. Vapour density, 7·523.

		Pelouze & Cahours.			Vol.	Density.
30 C	180	84·91	.. 84·71	C-vapour	30	12·4800
32 H	32	15·09	.. 14·96	H-gas	32	2 2376
$C^{30}H^{32}$	212	100·00	99·67	Vap. of $C^{30}H^{32}$	2	11·7176
					1	7·3588

Its reactions are similar to those of the hydrides of tri- and tetra-decatyl. *Chlorine.* converts it into chloride of pentadecatyl $C^{30}H^{31}Cl$, boiling at about 300°.

Page 237.

Kinic Acid. According to Zwenger & Himmelmann, *Ann. Pharm.* 129, 203) pyrocatechin and hydrokinone are always obtained by the dry distillation of kinic acid and its salts. Uloth's *ericinone* (*Ann. Pharm.* 111, 215) is identical with hydroquinone, as first pointed out by Hesse (*Ann. Pharm.* 114, 301). All plants of the ericaceous order, whose aqueous extracts yield hydrokinone by dry distillation, contain either kinic acid, or arbutin (xv. 419), both of which substances yield hydrokinone by dry distillation. *Pyrola umbellata* contains both kinic acid and arbutin.

Page 426.

Reactions of Morphine. (A. Husemann, *Ann. Pharm.* 128, 305 ; *Rép. Chim. pure*, 1863, p. 283).— The process recommended by J. Erdmann for the detection of morphine, which consists in dissolving the morphine in strong sulphuric acid containing nitric acid, whereby a violet-red colour is said to be produced, may be rendered much more certain and delicate by first dissolving the base in strong sulphuric acid, in the proportion of 0·002 to 0·004 grm. to 6 or 8 drops of the acid, and then adding a drop of nitric acid, whereupon, if the morphine-solution has been recently prepared, a rose-colour is produced, changing after a few seconds to yellow, then to greenish, and finally to brown. — If a small quantity of water be added to the solution of the morphine in sulphuric acid, so that the mixture becomes hot, the

colouring produced by the subsequent addition of nitric acid is of a much deeper carmine-red, and much more durable. — If the solution is heated for a few minutes to 100°—150°, the addition of a drop of nitric acid produces, after cooling, a splendid deep violet colour, which gradually disappears from the centre outwards, passing through blood-red. — If the temperature is raised above 150°, the liquid acquires of itself, at a certain moment, a violet-rose colour; at still higher temperatures, a dirty green colour is produced. On adding a drop of nitric acid, after cooling, the liquid immediately turns red, without passing through violet. — A solution of morphine in sulphuric acid, left to itself for 12 to 24 hours at ordinary temperatures, behaves as if it had been heated to 100°—150°.

Hypochlorite of soda, chlorine-water, and *chlorate of potash* exhibit with morphine the same reactions as nitric acid.

With regard to the sensibility of these reactions, Husemann finds that $\frac{1}{5}$th of a milligramme of morphine is sufficient to produce a very bright carmine colour; $\frac{1}{50}$ milligr. gives a very distinct reaction, and $\frac{1}{100}$ milligr. still gives a perceptible tint after half a minute.

A solution of morphine in sulphuric acid previously heated, is coloured deep-red by *sesquichloride of iron,* the colour changing after a while to dirty green (compare *Reactions of Narcotine,* p. 532).

Page 498.

Quercitrin-sugar or Isodulcite.

$C^{12}H^{12}O^{10}$.
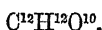
HLASIWETZ & PFAUNDLER. *Ann. Pharm.* 127, 362; *Rép. Chim. pure,* 1863, p. 204).

This sugar, isomeric with mannite and dulcite, is obtained (together with quercetin) by boiling quercitrin with dilute sulphuric acid, saturating with carbonate of baryta, and evaporating the filtrate to a thick syrup. The sugar is then deposited, after a few hours, in fine, nearly colourless crystals, which are obtained quite colourless by recrystallisation with aid of animal charcoal.

The crystals are identical in form with those of cane-sugar, taste sweeter than grape-sugar, dissolve in 2·09 pts. of water at 18°, also in hot absolute alcohol. The solution [? aqueous] exhibits a dextro-rotatory power of 0·0763°. The air-dried crystals contain 2 at. water. which they give off at 110°, melting at the same time.

	At 110°.		Hlasiwetz & Pfaundler.		Air-dried.		Hlasiwetz & Pfaundler.
12 C	....	72	43·90	43·55	12 C 72	39·56	39·38
12 H	....	12	7·32 .	7·44	14 H 14	7·69 ...	7·93
10 O	.... ..	80 ..	48·78	49·01	12 O 96	52·75 ...	52·69
$C^{12}H^{12}O^{10}$...	164	100·00	100·00		$C^{12}H^{14}O^{12}$.... 182	100·00	100·00

Different, therefore, from the quercitrin-sugar obtained by Rigaud (xv, 348). The authors are of opinion that there may be several varieties of quercitrin containing different sugars, and they remark that rutin (p. 500), robinin (p. 505), and perhaps

also rhamnin (p. 80), do not differ from quercitrin more than certain quercitrins differ one from the other.

Isodulcite does not appear to be *fermentable*. It is reduced by *hydriodic acid*, yielding an oily, ethereal iodine-compound. — It reduces *cupric oxide* from alkaline solutions, the reducing power of the crystals ($C^{12}H^{14}O^8$) being to that of grape-sugar as 5·288 to 5·000. — It is oxidised by *nitric acid*, yielding an acid analogous to saccharic acid (not mucic acid, like dulcite xv. 386), and only traces of oxalic acid.

Nitro-isodulcite $C^{12}H^9(NO^4)^3O^{10}$. Obtained by dissolving pulverised isodulcite in a mixture of nitric and sulphuric acids The solution takes place without evolution of gas, and after a short time the nitro-compound separates as a white viscous mass, which gradually hardens; the quantity increases on addition of water. It is soluble in alcohol, cannot be crystallised, melts below 100°, and detonates slightly under the hammer.

							Hlasiwetz and Pfaundler.
12 C	....	72	....	24 08	....	24 41
9 H	. ...	9	....	3·01	. .. .	3·05
3 N	....	42	....	14 04	....	14·21
22 O	.. ..	176	....	58 87	. ...	58·33
$C^{12}H^9(NO^4)^3O^{10}$		299	....	100·00	....	100 00

Isodulcite is distinguished from mannite and dulcite by its melting point (mannite melting at 160°, dulcite at 182°), by its action on polarised light, and by not forming a baryta-compound; from dulcite also by its reaction with nitric acid.

END OF VOL. XVI.

REPORT

THE FIFTEENTH ANNIVERSARY MEETING

CAVENDISH SOCIETY.

The Anniversary Meeting of the Cavendish Society for the year 1862, was held at the rooms of the Chemical Society, in Burlington House, on Saturday the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, Esq., F.R.S., President, who called upon the Secretary to read

THE REPORT OF THE COUNCIL.

" The Proceedings of the Cavendish Society being at present limited to the completion of the translation of GMELIN's Chemistry there are but few subjects to which the Council have to refer in this Report. They regret the delay which has occurred in bringing out the volume for 1861, a delay which they had not anticipated, and which has arisen from causes over which they have had no control. The new German edition of GMELIN has for several years been produced in parts, which have issued from the press with a degree of regularity that seemed to justify the conclusion that the English Editor might produce a volume of the translation, of the usual size, every year, and founded upon this conclusion the

fifteenth volume of the work was promised, and is due, for the year 1861. A portion of the matter for this volume, all in fact that remained of the last published German part, has for many months been prepared for the English edition, but as this was insufficient to complete the volume, it was necessary to wait for other German parts, one of which, although expected six months ago, has but recently arrived. This will furnish matter to proceed with, and when the requisite quantity is obtained to make a volume no time will be lost in supplying it to the members who have subscribed for 1861.

In a note appended to the part of the German work, just received, a promise is given that the entire work shall be completed in the course of the present year. Should this promise be fulfilled the sixteenth volume which will be issued for 1862, may be expected in the course of the following year. Considerable progress has been made in the preparation of a general Index, which will greatly enhance the value of the work for the purpose of reference.

The Council are happy to be able to announce the republication of the first volume of the Handbook, which was undertaken by Mr. HARRISON, without involving the Society in any responsibility. In the reprinting of this volume the matter has been carefully read and corrected by the Editor.* A few complete sets of the work may now be obtained from the Agent, and Members and others who have sets with the first volume deficient, may remedy the defect.

The financial position of the Society will, the Council trust, be considered satisfactory. There are no outstanding debts, or liabilities, while the balance at the Bank is sufficient to meet the cost of the completion of the volume due for last year. There is also a considerable stock in hand of some of the Society's works. The Council congratulate the Members upon this position of the affairs of the Society, and they hope that the steady and liberal support hitherto given to it will not be withdrawn until the objects for which it was founded shall be realized, one of the most important of which was the production of an English edition of GMELIN's Chemistry.

STATEMENT of RECEIPTS and EXPENDITURE of the CAVENDISH SOCIETY, from the 26th of February, 1861, to the 1st of March, 1862.

RECEIPTS.		£	s.	d.		£	s.	d.
Balance from previous year	..	283	4	1	Petty Cash ... penditure	10	1	7
1 Subscription for 1852	..	1	1	0	Agent for Distribution of Books, &c	40	0	0
1 Ditto 1855	..	1	1	0	Insurance	2	4	0
2 Ditto 1856	..	2	2	0	Commission to Collectors	18	15	9
5 Ditto 1857	..	5	5	0	Editorial Expenses	56	14	0
14 Ditto 1858	..	14	14	0	Paper	2	6	3
30 Ditto 1859	..	31	10	0	Printing	50	16	6
108 Ditto 1860	..	113	8	0	Binding and wrapping ..	25	2	4
195 Ditto 1861	..	204	15	0		406	0	0
14 Ditto 1862	..	14	14	0	Balance in hand .	375	5	5
52 American Subscriptions, nett	..	49	8	0				
Sale of Books	..	60	3	4				
		£78	5	5		£78	5	5

We have examined the above Statement and find it correct,

J. STENHOUSE,
W. ODLING.

March 1st, 1862.

It was resolved—

"That the Report just read be received, approved, and adopted."

The Meeting then proceeded to the election of Officers for the ensuing year, and the following Gentlemen were declared to have been duly elected:—

President.
THOMAS GRAHAM, F.R.S.

Vice-Presidents.

PROFESSOR BRANDE, F.R.S.
THE DUKE OF DEVONSHIRE, F.R.S.
WALTER CRUM, F.R.S.
JOHN DAVY, M.D., F.R.S.
CHARLES G. B. DAUBENY, M.D., F.R S.
MICHAEL FARADAY, D.C.L., F.R.S.
A. W. HOFMANN, Ph. D., LL.D., F.R.S.

HENRY BEAUMONT LEESON, M.D., F.R.S.
W. A. MILLER, M D , F.R.S.
ROBERT PORRETT, F.R.S.
A. W. WILLIAMSON, Ph.D. F.R S.
COLONEL PHILIP YORK, F.R.S.

Council.

DUGALD CAMPBELL, F.C.S.
P. J. CHABOT, M.A., F.R.A.S., F.C.S.
WARREN DE LA RUE, Ph.D., F.R.S.
W. FERGUSON, F.C.S.
E. FRANKLAND, Ph.D., F.R.S.
J H. GILBERT, Ph D., F.C.S.
DANIEL HANBURY, F.L S.
CHARLES HEISCH, F.C.S.

N. S. MASKELYNE, F.C.S.
WILLIAM ODLING, M.B., F.R.S.
ALFRED SMEE, F.R.S.
J. DENHAM SMITH, F.C.S.
JOHN STENHOUSE, LL.D., F.R.S.
R. D. THOMSON, M.D., F.R.S.
CHARLES TOMLINSON, ESQ.
A. W. WILLIAMSON, Ph. D., F.R.S.

Treasurer.
GEORGE DIXON LONGSTAFF, M.D., 9, Upper Thames Street.

Secretary.
THEOPHILUS REDWOOD, Ph. D, 19, Montague Street, Russell Square.

Collector.
MR. THOMAS WEST, Burlington House, Piccadilly, W.

Agent for the Distribution of Books, &c.
MR. F. HARRISON, 59, PALL MALL, S.W.

It was resolved—

"That MESSRS. BUCKTON and TRENHAM REEKS, and DR. GLADSTONE, be appointed Auditors for the ensuing year."

The following Resolutions were unanimously adopted:—

"That the thanks of the Meeting be given to the PRESIDENT, COUNCIL, and OFFICERS, for their services to the Society."

"That the thanks of the Meeting be given to the HONORARY LOCAL SECRETARIES for their services to the Society."

"That the thanks of the Meeting be given to the CHEMICAL SOCIETY for the use of their rooms."

THEOPHILUS REDWOOD, SECRETARY,
19, Montague St., Russell Square, & 17, Bloomsbury Square.

OBJECTS, &c., OF THE CAVENDISH SOCIETY.

The Cavendish Society was instituted for the promotion of Chemistry and its allied sciences, by the diffusion of the literature of these subjects.

The subscription, constituting membership, is one guinea a-year, to be paid in advance; and the subscription becomes due on the 1st of January of each year. A member is entitled to a copy of every book published by the Society for the year for which he has subscribed, but no member can receive the Society's publications until his subscription has been duly paid.

WORKS OF THE CAVENDISH SOCIETY.

CHEMICAL REPORTS AND MEMOIRS. Edited by Professor Graham. This work is out of print.

GMELIN'S HAND-BOOK OF CHEMISTRY. Translated and Edited by Henry Watts, B.A., F.C.S.

A few sets remain from Vol. I to Vol. XII, which are supplied for £6 6s. Separate copies of the Volumes from IV to XII may also be had at 10s. 6d. each.

Vols. XIII, XIV and XV can only be obtained by subscribing for the years for which they were issued.

LEHMANN'S PHYSIOLOGICAL CHEMISTRY. Translated and Edited by Dr. G. E. Day, F.R.S.

The First Volume of this work is out of print. There still remain a few copies of the Second and Third Volumes, and of Dr. Otto Funke's Atlas of Physiological Plates, which, together, may be obtained for £1 1s.

BISCHOF'S ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY.

The First and Second Volumes of this Work are supplied for a subscription of £1 1s.

THE LIFE AND WORKS OF CAVENDISH. By Dr. Geo. Wilson.

THE LIFE AND SCIENTIFIC RESEARCHES OF DALTON. By Dr. W. C. Henry, F.R.S.

LAURENT'S CHEMICAL METHOD. Translated by Dr. Odling.

These three Works are supplied for a subscription of £1 1s.

***** Applications for the works of the Cavendish Society, are to be made to the Agent, Mr. Harrison, 59, Pall Mall, S.W.; by whom also the Subscriptions of Members are received.

Honorary Local Secretaries.

Aberdeen—Dr. R. Rattray.

Banbury—Thomas Beesley, Esq.

Bath—J. P. Tylee, Esq.

Bathgate—James Young, Esq.

Beccles—W. E. Crowfoot, Esq.

Bedford—W. Blower, Esq.

Belfast—Dr. J. F. Hodges.

Birmingham—George Shaw, Esq.

Bolton—H. H. Watson, Esq.

Bradford—Robert Parkinson, Ph. D.

Brighton—F. Busse, Esq.

Bristol—Wm. Herapath, Esq.

Cambridge—W. H. Miller, Esq., M.A., F.R.S.

Chester—R. D. Grindley, Esq.

Clifton—G. F. Schacht, Esq.

Cork—Thomas Jennings, Esq.

Dublin—Dr. J. Apjohn.

Exeter—George Cooper, Esq.

Farnham—W. Newnham, Esq.

Galway—Dr. T. H. Rowney.

Glasgow—Walter Crum, Esq., F.R.S.

Gosport—Dr. W. Lindsay, R.N.

Guernsey—Dr. E. Hoskins, F.R.S.

Halifax—John W. Garlick, M.D.

Hull—Thomas J. Smith, Esq.

Leeds—W. S. Ward, Esq.

Liverpool—{ Dr. J. Dickinson.
J. B. Edwards, Ph. D.

Llandilo—B. Morgan, Esq.

Manchester—{ John Graham, Esq.
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York—W. G. Procter, Esq.

UNITED STATES.

New York—Henry Baillière, Esq., 290, Broadway.

Philadelphia—William Procter, jun., Esq.

CAVENDISH SOCIETY.

REPORTS

READ AT

THE FIFTEENTH, SIXTEENTH,

AND

SEVENTEENTH ANNIVERSARY MEETINGS.

REPORT OF THE COUNCIL.
(*Presented 1st March,* 1862.)

" The Proceedings of the Cavendish Society being at present limited to the completion of the translation of GMELIN's Chemistry, there are but few subjects to which the Council have to refer in this Report. They regret the delay which has occurred in bringing out the volume for 1861, a delay which they had not anticipated, and which has arisen from causes over which they have had no control. The new German edition of GMELIN has for several years been produced in parts, which have issued from the press with a degree of regularity that seemed to justify the conclusion that the English Editor might produce a volume of the translation, of the usual size, every year, and founded upon this conclusion the fifteenth volume of the work was promised, and is due, for the year 1861. A portion of the matter for this volume, all in fact that remained of the last published German part, has for many months been prepared for the English edition, but as this was insufficient to complete the volume, it was necessary to wait for other German parts, one of which, although expected six months ago, has but recently arrived. This will furnish matter to proceed with, and when the requisite quantity is obtained to make a volume, no time will be lost in supplying it to the members who have subscribed for 1861.

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REPORT OF THE COUNCIL.
(*Presented 1st March*, 1863.)

"The Council have but little to add on the present occasion to the statements contained in former reports. As explained at the last and preceding Anniversary Meetings, and with the concurrence of the Members then present, the proceedings of the Society are now, and have been for the last two or three years, limited to the completion of the translation of GMELIN's Chemistry, and this work is produced and supplied to the subscribers with as little interruption and delay as the circumstances attending the publication of the German edition of the work will admit. The fifteenth volume of the English edition was, at the date of the last Anniversary Meeting, partly prepared, and was then due for the previous year, but the Editor has not been able to complete it until recently, for want of sufficient matter. The past year has therefore been one of more than usual inactivity, and the Council have not thought it desirable to take any steps towards collecting subscriptions for the past year until the volume due for 1861 was issued. This is now ready, and sufficient matter for part of another volume has recently been received from abroad, in the translation of which the Editor is engaged; and he is of opinion that one other volume in addition to that now in hand, together with the Index, in the preparation of which some progress has been made, will bring this great work to a conclusion.

"As the receipts for the past year have chiefly consisted of payments which Members have proffered without application having been made to them, the amount has necessarily been small. The subscriptions received have amounted to £137 12s., while the expenditure, for editorial expenses, agency, paper, binding, &c., has amounted to £251 18s. 7d., leaving a balance in hand of £261 8s. 10d."

THE

SEVENTEENTH ANNIVERSARY MEETING

OF THE

CAVENDISH SOCIETY

Was held at the rooms of the Chemical Society, in Burlington House, on Saturday the 1st of March, 1864, at three o'clock in the afternoon.

THE MASTER OF THE MINT, President of the Society, in the Chair.

THE REPORT OF THE COUNCIL

was read as follows :—

"At the last Anniversary Meeting the Council announced the completion of the fifteenth volume of the Translation of GMELIN'S Chemistry, which was supplied to Members for 1861, and they expressed regret at the delay which attended the production of that volume, although it arose from causes over which they had no control. During the year that has since elapsed, another volume of the same work has been in preparation, and it is now nearly ready for publication. This constitutes the sixteenth volume of GMELIN, which will be issued in about a month from the present time, as a book for 1862. The Editor thinks that one more volume, in addition to that now in hand, will complete the work, with the exception of the Index, which is also in hand.

A reference to previous reports and to resolutions passed at meetings at which the position of the Society and the progress made in the work it had undertaken have been fully discussed, will serve to explain the causes of the comparative inactivity which has marked the proceedings of the Society for several years past. It is unnecessary to repeat here what has already been said, beyond simply stating that the operations of the Society are now confined to the completion of the translation of GMELIN'S Chemistry, and that the progress made with that work is necessarily limited by the rate at which the German Edition is produced.

When the Council found that the German work was not produced sufficiently fast to enable the English Editor to prepare a volume of the translation every year, they refrained from applying to the Members for their subscriptions during the delay that occurred in supplying the books; and on this account the accompanying Financial Statement gives the receipts and expenditure for the last two years, during which time only one volume has been issued.

The Council hope, and believe, that when the subscriptions are paid up for the present year (1864), there will be funds enough in hand to defray all the expenses of the Society attending the completion of their great and now only remaining unfinished work, and including the Index to that work.

STATEMENT of Receipts and Expenditure of the CAVENDISH SOCIETY, from the 1st March, 1862, to 1st March, 1864.

RECEIPTS.				EXPENDITURE.			
	£	s.	d.		£	s.	d.
Balance in hand on March, 1862	375	15		Petty Cash	1	18	0
2 Subscriptions for 1855	2	2	0	Agent for Distribution of Books, &c. (2 years)	80	0	0
2 Ditto. 1856	2	2	0	Insurance (2 years)	4	8	0
9 Ditto 1857	9	9	0	Commission to Collector	12	9	9
25 Ditto 1858	26	5	0	Editorial Expenses	210	17	6
38 Ditto 1859	39	18	0	Paper	67	0	7
39 Ditto 1860	40	19	0	Printing	159	14	6
47 Ditto 1861	49	7	0	Binding	34	5	3
147 Ditto 1862	154	7	0		£570	13	7
32 Ditto 1863	33	12	0				
1 Ditto 1864	1	1	0	Balance in hand	220	1	4
Sale of Books	55	17	6				
	£790	14	11		£790	14	11

March 1st, 1864.   Examined and found correct
                                           HENRY DEANE.

It was resolved—

"That the Report just read be received, approved, and adopted."

The Meeting then proceeded to the election of Officers for the ensuing year, and the following were duly elected:—

President.

THOMAS GRAHAM, F.R.S.

Vice-Presidents.

PROFESSOR BRANDE, F.R.S.
SIR BENJAMIN BRODIE, F.R.S.
WALTER CRUM, F.R.S.
THE DUKE OF DEVONSHIRE, F.R.S.
MICHAEL FARADAY, D.C.L., F.R.S.
A. W. HOFMANN, Ph.D., LL.D., F.R.S.

HENRY BEAUMONT LEESON, M.D., F.R.S.
W. A. MILLER, M.D., F.R.S.
ROBERT PORRETT, F.R.S.
WILLIAM SHARPEY, M.D., F.R.S.
A. W. WILLIAMSON, Ph.D., F.R.S.
COLONEL PHILIP YORK, F.R.S.

Council.

G. B. Buckton, F.R.S.
Dugald Campbell, F.C.S.
Philip James Chabot, M.A., F.R.A.S. F.C.S.
Rev. T. P. Dale.
Warren De La Rue, Ph. D., F.R.S.
E. Frankland, Ph. D., F.R.S.
J. H. Gilbert, Ph.D., F.R.S.
J. H. Gladstone, Ph.D., F.R.S.

Daniel Hanbury, F.L.S.
Charles Heisch, F.C.S.
J. B. Lawes, F.R.S.
William Odling, M.B., F.R.S.
J. Denham Smith, F.C.S.
John Stenhouse, LL.D., F.R.S.
R. D. Thomson, M.D., F.R.S.
Charles Tomlinson, F.C.S.
A. W. Williamson, Ph.D., F.R.S.

Treasurer.

George Dixon Longstaff, M.D., 9, Upper Thames Street.

Secretary.

Theophilus Redwood, Ph.D., 19, Montague Street, Russell Square.

Collector.

Mr. Thomas West, Burlington House, Piccadilly, W.

Agent for the Distribution of Books, &c.

Mr. F. Harrison, 59, Pall Mall, S.W.

It was resolved—

"That W. Crookes, Esq., Dr. Letheby, and G. H. Makins, Esq., be appointed Auditors for the ensuing year."

The following Resolutions were unanimously adopted:—

"That the thanks of the Meeting be given to the President, Council, and Officers for their services to the Society."

"That the thanks of the Meeting be given to the Honorary Local Secretaries for their services to the Society."

"That the thanks of the Meeting be given to the Chemical Society for the use of their rooms."

THEOPHILUS REDWOOD, Secretary,
19, Montague St., Russell Square, & 17, Bloomsbury Square.

March, 1864.

OBJECTS, &c., OF THE CAVENDISH SOCIETY.

THE Cavendish Society was instituted for the promotion of Chemistry and its allied sciences, by the diffusion of the literature of these subjects.

The subscription, constituting membership, is one guinea a-year, to be paid in advance; and the subscription becomes due on the 1st of January of each year. A member is entitled to a copy of every book published by the Society for the year for which he has subscribed, but no member can receive the Society's publications until his subscription has been duly paid.

WORKS OF THE CAVENDISH SOCIETY.

1848.

1.—CHEMICAL REPORTS AND MEMOIRS. Edited by Thomas Graham, F.R.S. (Out of Print.)
2.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Translated by Henry Watts, B.A., F.C.S. Vol. I.

1849.

3.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. II.
4.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. III.
5.—THE LIFE AND WORKS OF CAVENDISH. By Dr. George Wilson.

1850.

6.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. IV.
7.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. V.

1851.

8.—PHYSIOLOGICAL CHEMISTRY. By Professor Lehmann. Translated by George E. Day, M.D., F.R.S. Vol. I. (Out of Print.)
9.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. VI.

1852.

10.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. VII. (Organic Chemistry, Vol. I.)
11.—PHYSIOLOGICAL CHEMISTRY. By Professor Lehmann. Vol. II.
12.—ATLAS OF PLATES RELATING TO PHYSIOLOGICAL CHEMISTRY. By Dr. Otto Funke. (Supplement to Lehmann's Physiological Chemistry.)

1853.

13.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. VIII. (Organic Chemistry, Vol. II.)
14.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY. By Professor Bischof. Vol. I.

1854.

15.—THE LIFE AND SCIENTIFIC RESEARCHES OF DALTON. By Dr. W. C. Henry, F.R.S.
16.—PHYSIOLOGICAL CHEMISTRY. By Professor Lehmann. Vol. III.
17.—LAURENT'S CHEMICAL METHOD. Translated by Wm. Odling, M.B.

1855.

18.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. IX. (Organic Chemistry, Vol. III.)
19.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY. By Professor Bischof. Vol. II.

CHEMICAL REPORTS AND MEMOIRS. Edited by Professor
Graham. This work is out of print.

GMELIN'S HAND-BOOK OF CHEMISTRY. Translated and
Edited by Henry Watts, B.A.. F.C.S.
Volumes II and III are out of print.
Separate copies of Volume I and Volumes IV to XII may be had at
10s. 6d each.
Vols. XIII, XIV, XV, and XVI can only be obtained by subscribing for
the years for which they were issued.

LEHMANN'S PHYSIOLOGICAL CHEMISTRY. Translated and
Edited by Dr. G. E. Day, F.R.S.
The First Volume of this work is out of print. There still remain a
few copies of the Second and Third Volumes, and of Dr. Otto Funke's
Atlas of Physiological Plates, which, together, may be obtained for
£1 1s.

BISCHOF'S ELEMENTS OF CHEMICAL AND PHYSICAL
GEOLOGY.
The First and Second Volumes of this Work are supplied for a sub-
scription of £1 1s.

THE LIFE AND WORKS OF CAVENDISH. By Dr. Geo. Wilson.

THE LIFE AND SCIENTIFIC RESEARCHES OF DALTON.
By Dr. W. C. Henry, F.R.S.

LAURENT'S CHEMICAL METHOD. Translated by Dr. Odling.
These three Works are supplied for a subscription of £1 1s.

*** Applications for the works of the Cavendish Society are to
be made to the Agent, Mr. Harrison, 59, Pall Mall, S.W.; by whom
also the subscriptions of Members are received.

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Banbury—Thomas Beesley, Esq.
Bath—J. P. Tylee, Esq.
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